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I.—*On Biniodacetic Acid.*

By W. H. Perkin, F.C.S., and B. F. Duppa, Esq.

In the number of "The Philosophical Magazine" for July last we gave an account of the formation and properties of iodacetic acid, which, it will be remembered, was prepared by acting on bromacetic ether with an alcoholic solution of iodide of potassium, the result of which action was iodocetic ether. This, in its turn, was treated with baryta water, and the resulting barium salt decomposed by sulphuric acid. Since then we have discovered that, by treating bibromacetic ether in a similar manner, biniodacetic acid is formed. We shall now proceed to describe the process we employed for the preparation of this interesting substance from biniodacetic ether, which will be described hereafter.

Biniodacetate of ethyl is decomposed best by shaking it up in a flask with a small quantity of milk of lime, small additions of the latter being made continually until no further smell of the ether can be perceived, or any burning sensation produced on the tongue when a small quantity of the liquid is applied. The mixture of hydrate of calcium and the solution of the new salt is placed on a filter, and well washed—first with cold, and then with hot water—until the liquid, passing through, no longer gives a precipitate of

iodide of silver when gently heated with a drop of acid nitrate. The liquid containing biniodacetate and hydrate of calcium and alcohol in solution is then very gently evaporated until it just begins to crystallize. The object of this is to ensure the complete volatilization of the alcohol which was present, as it interferes much with the precipitation of the acid, and has, moreover, a tendency to decompose it. Should any crystals exist in the liquid, a small quantity of water must be added, to bring them in solution. The liquid being cold, dilute hydrochloric acid is added (strong acid decomposes, and also dissolves the acid, as it is separated from its calcium salt)—in sufficient quantity to liberate the acid, and no more. This is known by no further turbidity being produced when more acid is added to a drop on a watch-glass. The milky liquid is now left at rest, when the acid begins to shoot out into a confused mass of crystals. At the bottom of the vessel is generally found a large portion of the acid in the form of a heavy yellow oil, which, after a time, concretes into a mass of large, opaque, sulphur-yellow rhombohedrons. The crystals are repeatedly washed with a little cold water, and dried.

The acid, thus prepared, is a beautifully crystalline sulphur-yellow substance, having a slightly acid and metallic after-taste. It does not act on the skin like the corresponding bromine-compound. It is but slightly soluble in water. Crystals of the acid exposed to the air slowly disappear, being volatile at the common temperature.

On opening a bottle containing crystals of the acid, a faint smell, resembling iodine, manifests itself. Heated on platinum foil, it fuses partly, volatilizes, and then turns black, evolving copious fumes of iodine.

All the salts of this acid we have yet examined are slightly yellow: all crystalline and permanent, with the exception of those of potassium and sodium, which are deliquescent.

Biniodacetate of calcium crystallizes in silky needles of a yellow colour; heated on platinum foil, it evolves iodine.

Biniodacetate of barium is a crystalline salt, forming large rhombohedral crystals of a pale yellow colour, tolerably soluble in water, and giving off iodine when heated. A combustion of a portion, dried in vacuo over sulphuric acid, gave the following results:

·7473 of substance gave
·1605 of carbonic acid and
·0388 of water.

These numbers agree with the formula,

$$Ba,C_4(HI_2)O_4$$

as may be seen by the following table:—

			Theory.		Mean of Experiment.
Carbon	4 equivs.	.	24·00	6·32	5·85
Hydrogen	1 „	.	1·00	·26	·57
Barium	1 „	.	68·59	18·07	—
Iodine	2 „	.	253·76	66·86	—
Oxygen	4 „	.	32·00	8·49	—
			379·35	100·00	

Biniodacetate of Lead.—This salt is best prepared by adding a solution of diïodacetate of sodium to a solution of acetate of lead, both being largely diluted. After a few moments, the mixture becomes turbid, and a considerable quantity of a crystalline precipitate rapidly forms, which must be well washed with cold water, in which it is nearly insoluble; when dry, it is of a pale yellow colour, and, seen under the microscope, is found to consist of minute prismatic crystals. The following analyses were made:

I. ·5052 of substance gave
·1054 of carbonic acid, and
·0335 of water.

II. ·3695 of substance gave
·0774 of carbonic acid, and
·0200 of water.

III. ·3223 of substance gave
·0675 of carbonic acid, and
·0148 of water.

IV. ·5667 of substance gave
·2035 of sulphate of lead.

Percentage composition:—

		I.	II.	III.	IV.
Carbon	. .	5·68	5·71	5·71	—
Hydrogen	.	·673	··43	·51	—
Lead	. .	—	—	—	24·53

These numbers agree with the formula,

$$Pb,C_4(HI_2)O_4,$$

as may be seen from the subjoined table:—

			Theory.		Mean of Experiments.
Carbon	4 equivs.	.	24·	5·79	5·7
Hydrogen	1	..	1·	·26	·57
Iodine	2	..	253·76	61·24	—
Oxygen	4	..	32·	7·72	—
Lead	1	..	103·57	24·99	24·53
			414·33	100·00	

Biniodacetate of Silver.—This salt is produced by adding a neutral solution of nitrate of silver to one of düodacetate of sodium. It is best to use dilute solutions, as the precipitate forms more slowly and more perfectly crystallized. The precipitate must be well washed with cold water, and dried in vacuo. It is a yellow crystalline powder, decomposed when gently heated on platinum foil, the decomposition being attended with a slight explosion, one equivalent of iodine being evolved.

This salt, when boiled, readily splits up into iodide of silver and iodoglycolic acid.

The following silver, iodine, and carbon and hydrogen determinations were made:—

I. ·1215 of substance gave
·2350 of iodide of silver.

II. ·8970 of substance gave
·2313 of iodide of silver.

III. ·3350 of substance gave
·3720 of iodide of silver.

IV. .4022 of substance gave
·1510 of iodide of silver, and
·1363 of chloride of silver.

V. ·5130 of substance gave
·1159 of carbonic acid, and
·0148 of water.

Percentage composition:—

	I.	II.	III.	IV.	V.
Carbon	—	—	—	—	5·82
Hydrogen	—	—	—	—	·30
Iodine	—	—	59·98	60·57	—
Silver	25·45	25·78	—	25·50	—

These numbers agree with the formula,

$$Ag, C_4 \, H I_2 \, O_4$$

as may be seen from the following table :—

			Theory.		Mean of Experiments.
Carbon	4 equivs.	.	24·00	5·73	5·82
Hydrogen	1 ,,	.	1·00	·23	·30
Iodine	2 ,,	.	253·76	60·52	60·27
Silver	1 ,,	.	108·00	25·78	25·57
Oxygen	4 ,,		32·00	7·74	—
			418·76	100·00	

Biniodacetate of Ethyl.—To prepare this substance, a distilling and condensing apparatus, like that used for the preparation of pure tannin, is convenient, the iodide of potassium being placed in the large tube, and the bibromacetic ether, previously mixed with three times its volume of alcohol, in the flask. The apparatus is then placed on a water-bath, and the contents kept boiling until all the iodide of potassium has dissolved by the constant filtration of the alcohol through it. The iodide should be used in the proportion of two equivalents to one of bibromacetic ether. The flask is then detached, a bent tube fitted to it, and the contents distilled until all the alcohol has passed over, which may be known by the liquid coming over turning milky. The flask is then opened, and a drop of the oily liquid at the bottom tested with a little ammonia, which immediately converts it into the amide, which, when heated with a little oxide of manganese and sulphuric acid, gives off iodine. Should the vapour not be good in colour, and the crystals soft, it is a sign that some bibromacetic ether is still undecomposed, and that the digestion with alcohol must be renewed until the test gives pure-looking iodine vapours. The flask, when the reaction is terminated, is emptied of its contents into a test-glass, and the oil at the bottom taken up with a pipette, and well washed with water. A little mercury is then shaken up with it, when the dark colour of the dissolved iodine will in a few moments vanish.

Thus prepared, biniodacetic ether is a yellowish liquid, having a pungent burning taste, and irritating the eyes and nose in a powerful manner. It is insoluble, or nearly so, in water: ammonia rapidly converts it into biniodacetamide.

We have not made an analysis of this substance, as the

reactions we obtained were so clearly definite that we did not consider it necessary.

Biniodacetamide.—As mentioned before, this substance is produced when a solution of ammonia is brought in contact with the above-mentioned ether. It is a difficultly soluble substance, of a pale yellow colour. The following analyses were made:

I. ·5910 substance gave
·1788 of carbonic acid, and
·0593 of water.

II. ·3400 of substance gave
·0995 of carbonic acid, and
·0362 of water.

III. ·5303 of substance gave
·3972 of chloroplatinate of ammonium.

Percentage composition:—

	I.	II.	III.
Carbon . .	8·25	7·98	—
Hydrogen . .	1·11	1·18	—
Nitrogen . .	—	—	4·68

which agree with the formula,

$$C_4(H_3I_2)NO_2,$$

as may be seen by the subjoined table:—

		Theory.		Mean of Experiment.
Carbon	4 equivs. .	24·00	7·72	8·11
Hydrogen	3 ,, .	3·00	·96	1·14
Iodine	2 ,, .	253·76	81·65	—
Nitrogen	1 ,, .	14·00	4·52	4·68
Oxygen	2 ,, .	16·00	5·15	—
		310·76	100·00	

Having experienced great difficulties in making iodine determinations, we beg to be allowed to mention the method we pursued in obtaining the numbers mentioned in this paper.

After having tried all the methods detailed in the manuals, it occurred to us that possibly the iodine might be eliminated from biniodacetic acid by means of nascent hydrogen. The first object to be obtained was the perfect solution of a salt in some liquid without heat. For this purpose we selected the silver salt, mixed it with water, and added a few drops of ammonia, which immediately produced a clear solution. We then added metallic zinc,

which directly precipitated the silver in the metallic form, rendering the liquid yellow from a small quantity of iodide of silver that was formed. A few moments' stirring decomposed this, and the liquid became perfectly clear. The metallic zinc and silver were then separated by means of a filter, and repeatedly washed with water, to which a few drops of ammonia had been added, to keep oxide of zinc in solution. The solution was then treated in the ordinary way with nitric acid and nitrate of silver for precipitation of the iodine.

II.—*Description of an hermetically sealed Barometer.*

By Richard Adie, Liverpool.

When mounted on an ivory scale, this instrument resembles in size and portability a pocket thermometer of the medium or larger class.

It is constructed from a piece of thermometer tube, in which, in lieu of the spherical or cylindrical bulb formed for a thermometer, a cistern is made in the form of the section of a cylinder, 1·4 inches diameter and 1-10th of an inch thick, varying these measures according to circumstances; but generally the bulb has nearly the shape and dimensions of a half-crown. On the top of the tube there is an air cavity similar to that used in Dr. Rutherford's registering thermometer.

A. The cistern containing alcohol.

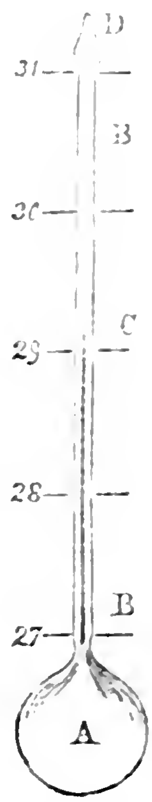
BB. The tube in which the height corresponding to the barometer is read.

C. The top of the alcohol column.

D. The air-cavity for correcting for temperature.

31 to 27. The figures to represent the height of the column C. with reference to the mercurial column.

Sub-divisions between each inch are added so as read off to ·02.



The influence of change of temperature is got rid of by trial and adjustment of each instrument; so that the expansion of the air in the upper cavity will counterbalance the expansion of the liquid in the cistern. This correction for temperature applies only to the condition of equal heating of the instrument throughout. When it is well done, an instrument is obtained, which is extremely sensitive to any change of atmospherical pressure.

If dipped in water at the temperature of the air, the column in the tube immediately rises to show the increase of pressure. When carried from one story of a house to another, the change is noticed as the stairs are ascended. In the beginning of last April, I put one of the barometers in the corner of the compartment of the railway carriage in which I was travelling, from Liverpool to Edinburgh, where it indicated regularly the extensive changes from the sea level which that line of route contains.

The hermetically-sealed barometer which I have found to work best is filled with coloured alcohol; the column in the tube moving through about 1·5 inches for every inch of the mercurial barometer.

Filled with mercury, instruments corrected for temperature were obtained to move through half an inch for every inch of the barometer; but, in point of mobility, they were much inferior to alcohol-filled tubes.

Filled with ether, an instrument corrected for temperature could not be obtained in combination with delicacy of indication; but if the correction for temperature be dispensed with, and a place can be found for the barometer where the changes of temperature are small, ether, in an hermetically-sealed tube of the kind described, would furnish a most minute measure of changes in atmospheric pressure.

A tube filled with water did not act with delicacy, from the want of mobility in the fluid.

In the hermetically sealed barometer, the reading may be much disturbed by unequal heating, when the instrument is held in the hand, or the sun allowed to shine on a portion of it. This can in a degree be prevented by the skill of the observer, with the interposition of non-conductors, and when carried by holding the instrument suspended by a cord, rather than keeping it in the pocket or hand. When the indication has been disturbed by unequal heating, it must remain suspended fifteen or twenty minutes before a reliable reading can be made.

III.—*Action of Pentachloride of Phosphorus on Tartaric Acid.*

By W. H. Perkin, F.C.S. and B. F. Duppa, Esq.

In a paper on malic acid, published last April in the Philosophical Magazine, we mentioned that we were engaged with the study of the influence of pentachloride of phosphorus on Tartaric acid; our time, however, having been much occupied by other subjects, we have as yet been unable to investigate the matter thoroughly, but, having obtained some peculiar results, we take this opportunity of laying them before the Society.

On gently heating a mixture of pentachloride of phosphorus and tartaric acid, hydrochloric acid is evolved in abundance, and a perfectly liquid mixture is formed consisting of oxychloride of phosphorus and an oil. To obtain the latter in quantity we have found it best to operate in the following manner.

One part of pulverized tartaric acid and five or six of pentachloride of phosphorus are mixed and introduced into a retort and gradually heated until perfectly liquid. The temperature is then elevated and the liquid allowed to distil until it reaches 120°; it is maintained at this point, and dry air passed through the remaining liquid for five or ten minutes, so as to separate as much of the remaining oxychloride of phosphorus as possible.

This product, which is the chloride of a diatomic acid radical, sinks as an oil, when thrown in water, and gradually dissolves. It also dissolves in alcohol, forming an ethereal body. If projected into strong aqueous ammonia, a violent action ensues, chloride of ammonia and a new crystalline compound, very soluble in alcohol and water, being produced. With phenylamine this body reacts most energetically. It decomposes partially on being distilled.

As mentioned above, this substance gradually dissolves in water. If a considerable quantity is mixed with water, it becomes warm, and, on cooling, deposits a white, slightly crystalline acid. If exposed to the moist atmosphere for a day or two, it becomes a white solid mass.

This acid, after being well pressed between bibulous paper and recrystallized from water, presents itself as a white, almost amorphous, mass: but, when viewed under the microscope, appears as small transparent needles. It is very soluble in water and alcohol,

has a very acid taste, melts when heated, and solidifies into a crystalline mass on cooling. It is bibasic.

Acid potassium-salt. This is best obtained by taking a solution of the acid and dividing it into two equal portions, neutralizing one with carbonate of potassium and then adding the other to it. If not too dilute, the new salt immediately makes its appearance as a crystalline precipitate, which, after washing with cold water and recrystallizing once or twice, is obtained quite pure. It crystallizes in plates. It is more soluble than the acid tartarate of potassium. It contains chlorine. The following carbon, hydrogen, chlorine, and potassium determinations have been made:

I. ·3290 of substance gave
·3033 of carbonic acid, and
·0329 of water.

II. ·2064 of substance gave
·1567 of chloride of silver.

III. ·69525 of substance gave
·271 of chloride of potassium.

Percentage composition:—

Carbon	25·14
Hydrogen	1·11
Chlorine	18·82
Potassium	20·45

which agrees with the formula $KH,C_8(HCl)O_8$ as may be seen from the following table:—

		Theory.		Exp.
Carbon	8 equiv.	48	25·4	25·14
Hydrogen	2 ,,	2	1·05	1·11
Chlorine	1 ,,	35·5	18·81	18·82
Potassium	1 ,,	39·2	20·77	20·45
Oxygen	8 ,,	64·0	33·97	
		188·7	100·00	

The *neutral potassium-salt* is crystalline, and much more soluble than the former.

Silver-salt.—On adding nitrate of silver to a solution of either of the above salts, a white precipitate is immediately formed, this, when washed with cold water and dried in vacuo over sulphuric acid is fit for analysis. It is very slightly soluble in water. When viewed under a powerful lens, it presents a slightly crystalline appearance. On being heated on platinum foil, it decrepitates, leaving a residue of metallic silver and chloride of silver. The subjoined determinations were made :—

I. ·2655 of substance gave
·210 of chloride of silver.

II. ·29325 of substance gave
·17375 of metallic silver, and
·117 of chloride of silver.

Percentage composition :—

	I.	II.
Silver	59·5	59·25
Chlorine	——	9·50

These numbers agree with the formula $Ag_2,C_8(HCl)O_8$ as may be seen from the following table :—

		Theory.		Exp.
Carbon	8 equiv.	48	13·16	——
Hydrogen	1 ,,	1	·27	——
Chlorine	1 ,,	35·5	9·74	9·50
Silver	2 ,,	216·0	59·23	59·37
Oxygen	8 ,,	64·0	17·60	——
		364·5	100·00	

Lead-salt. This salt is obtained by adding acetate of lead to a solution of the potassium salt. It is a crystalline substance difficultly soluble in water.

From the foregoing it evidently appears that the new acid has the composition $C_8(H_3Cl)O_8$, and the chloride from which it is derived, the formula $C_8(HCl)O_4,Cl_2$. This acid in composition represents maleic or fumaric acid, in which one equivalent of hydrogen is replaced by chlorine; but, as it is a very soluble substance, it would appear that if derived from either of the above, it would be from maleic acid, therefore we give it the provisional

name of *chloromaleic acid.* We hope shortly to be able to replace the chlorine in this acid by hydrogen, and then to ascertain whether it might be viewed as a derivative of maleic acid or not, because this is important, as it may show us the relation which tartaric acid bears to malic.

The action of pentachloride of phosphorus may be explained thus:—

$$\underbrace{C_8H_6O_{12}}_{\text{Tartaric acid.}} + PCl_5 = \underbrace{C_8H_4O_{10}}_{\text{Anhyd. tart. acid.}} + PCl_3O_2 + 2HCl.$$

Then—

$$C_8H_4O_{10} + 3PCl_5 = \underbrace{C_8(HCl)O_4.Cl_2}_{\text{New chloride.}} + 3PCl_3O_2 + 3HCl.$$

This appears to show that tartaric acid represents four molecules of water and that part of the hydrogen and oxygen exist in the same peculiar condition as in glycolic and lactic acid.

The formula of tartaric acid appears to be $\left.\begin{matrix}C_8H_2O_4\\H_4\end{matrix}\right\}O_8$

We have obtained some very interesting substances by digesting the bromacetic ethers with sulphocyanides, acetates, succinates, &c., the study of which we are now engaged with.

IV.—*On the Application of Electrolysis to the Detection of the Poisonous Metals in Mixtures containing Organic Matters.*

By Charles L. Bloxam.

Every analyst is only too well aware of the difficulties which beset the detection of the poisonous metals in mixtures containing organic matters, such as the contents of the stomach, the solids and fluids of the body, and articles of food.

The process which, I believe, most chemists now generally adopt in such cases, consists in disintegrating and partly oxidising the organic matters, by the aid of a mixture of hydrochloric acid and chlorate of potassa, and afterwards precipitating the filtered solution by hydrosulphuric acid, the arsenic acid having been previously reduced by means of sulphurous acid.

In most cases, the solution obtained by treating the organic

matters with hydrochloric acid and chlorate of potassa affords a precipitate on the passage of hydrosulphuric acid, whether any of the metals forming insoluble sulphides be present or not: this precipitate is generally of a dark greyish brown colour; is very difficult to filter and wash; and interferes in a most disagreeable manner with the application of the tests for those metals which are precipitable by hydrosulphuric acid from their acid solutions.

It is therefore in the highest degree desirable to adopt some more satisfactory method for separating the metals of the hydrosulphuric acid group from organic mixtures.

Two of these metals, arsenic and antimony, may, it is true, be readily extracted in the form of gaseous hydrogen compounds, by Marsh's process; and the objections to this course have been so often commented on, that, when I repeat some of the most important of them here, it is only that I may plead a fair excuse for submitting this communication to the society.

The occasional presence of arsenic in the sulphuric acid, and of both arsenic and antimony in the zinc, has always been a serious objection to the use of Marsh's test; and although the hydrogen evolved at the beginning of the experiment may be carefully examined before introducing the suspected liquid, the operator always proceeds upon the assumption that the zinc is perfectly homogeneous, and that it is impossible for arsenic or antimony, which had eluded detection in the first portion of hydrogen evolved, to become apparent when the mass of the zinc has entered into solution.

When liquids holding organic matters in solution are introduced into Marsh's apparatus, the frothing occasioned by the viscidity of the mixture often gives rise to very serious inconvenience; for although it may generally be checked by the addition of alcohol, it sometimes gets quite beyond the control of the operator, and the experiment is entirely lost.

But the most serious objection is that the liquid which has been examined by this method for arsenic and antimony cannot be examined for any other metals, on account of the presence of so large a quantity of sulphate of zinc, a consideration of very grave importance in cases where the quantity of the suspected matter is small.

The objections to the convenient and delicate process of Reinsch rest upon similar grounds, and are even more readily admissible.

The detection of the poisonous metals by the decomposing action of the galvanic current, is, I think, free from these objections, and so minute quantities of the poisonous metals may be detected by this method of testing, that it may safely be relied upon in most cases of chemico-legal investigations.*

The first experiments were directed to ascertain whether minute quantities of the most important poisonous metals could be easily detected, by electrolysis, in solutions free from organic matters.

Detection of Arsenic.

The apparatus which was at first employed, consisted of an ordinary U-tube, one limb of which was closed with a perforated cork through which passed a tube for the escape of the hydrogen, and a platinum wire connected with the zinc extremity of a Grove's battery of five cells; to this wire was attached a platinum plate, measuring about 2 inches by $\frac{3}{4}$ inch, which was thrust down almost to the bottom of the U-tube. The other limb of this tube was left open for the escape of the oxygen, and contained a similar platinum plate, connected with the platinum extremity of the battery.

The tube which carried off the hydrogen was connected with a straight tube of hard glass drawn out to a long open point, and heated to redness at the shoulder in order that any arseniuretted hydrogen might be decomposed in passing through it.

At the commencement of each experiment, the U-tube was charged with a fluid ounce of diluted sulphuric acid (containing one measure of oil of vitriol and four measures of water), and as soon as the closed limb had become filled with hydrogen, the drawn-out tube was heated with a spirit-lamp for 15 minutes in order to ascertain that no deposit of arsenic was obtained from the sulphuric acid alone. The solution to be examined for arsenic was then introduced into the closed limb, by withdrawing the cork for an instant, and the experiment continued.

The U-tube was immersed in a vessel of water to prevent the temperature from rising too high during the passage of the current.

* Before submitting this communication to the Society, the author was not aware of the existence of M. Gaultier de Claubry's admirable paper upon this method (J. Pharm. [3], xviii, 125; *abstr.* Chem. Soc. Qu. J. iii, 162). This chemist, however, appears to have relied upon the precipitation of the arsenic, not upon its evolution in the form of arseniuretted hydrogen.

The quantity of arsenic employed for each experiment was determined by carefully measuring out a standard solution of arsenious acid.

Three experiments made with aqueous solutions containing $\frac{1}{10}$, $\frac{1}{100}$ and $\frac{1}{1000}$ grain, respectively (corresponding to ·076, ·0076 and ·00076 grain of metallic arsenic), proved that the arsenic could be readily obtained, as in Marsh's test, in the form of a brilliant metallic crust in the narrow point of the tube, about half an inch beyond the heated portion.

In order to ascertain whether the presence of alcohol would interfere with the action of the test, in case it might become necessary to add it in order to prevent frothing, an ounce of dilute sulphuric acid and a drachm of alcohol were introduced into the apparatus and electrolysed until the tubes were full of hydrogen; on heating the evolution tube, a faint odour resembling mercaptan was perceived, but there was not the slightest deposit. On introducing $\frac{1}{100}$ grn. of arsenious acid, a most satisfactory mirror was formed in the tube in less than five minutes, and a decidedly arsenical odour, like that of alkarsin, proceeded from the extremity of the evolution tube.

In subsequent experiments, as in this, I found that the presence of alcohol appeared to facilitate the production of an arsenical crust, and that the arsenical odour afforded a valuable confirmation with respect to the presence of arsenic.

The method was then tested as to its applicability in cases where the arsenious acid is mixed with large quantities of organic matters.

A mixture was prepared, containing about 1 oz. lean meat, 1 oz. bread, $1\frac{1}{2}$ oz. milk and $\frac{1}{2}$ oz. white of egg, beaten to a pretty uniform pulp in a mortar. To this mixture was added an aqueous solution of $\frac{1}{10}$ grain of arsenious acid. The whole was then mixed with 1 fluid oz. of hydrochloric acid and 4 oz. of water; this mixture was digested in the water-bath for 15 minutes, filtered, and the clear solution evaporated on the water-bath to $3\frac{1}{4}$ fluid oz. of a dark brown viscid liquid.

On introducing one-fourth of this (= 0·025 grn. AsO_3) into the decomposing tube, it frothed up very much, but was immediately checked by the addition of a drachm of alcohol, and a deposit of arsenic was almost immediately formed in the heated tube.

A repetition of the experiment gave a similar result, but about 15 minutes were required for the formation of a good arsenical mirror.

In a third trial, one-sixth of the solution was taken ($=0{\cdot}017$ grn. AsO_3), with a like result, the odour of alkarsin being also very distinct.

A fresh organic mixture was poisoned, as before, with $\frac{1}{10}$ grn. of arsenious acid, and treated in the same manner, being finally evaporated to 2 fluid oz.

One-tenth of this opaque brown liquid ($=0{\cdot}01$ grn. AsO_3) gave a very distinct mirror in less than 5 minutes, attended with a strong arsenical odour.

One-hundredth of this liquid ($= 0{\cdot}001$ grn. AsO_3) also gave a very distinct mirror and odour in 10 minutes.

Since arsenic is sometimes contained in organic mixtures in a form (*e. g.* that of sulphide of arsenic) not readily soluble in hydrochloric acid, it became necessary to ascertain whether the solution obtained by adding chlorate of potassa together with the acid, would give the indication of arsenic by this method of testing: for such a solution would of course contain the arsenic in the form of arsenic acid.

The experiments made to determine this point proved that small quantities of arsenious acid ($\frac{1}{20}$ grn.) could not be detected by this test after boiling with hydrochloric acid and chlorate of potassa, unless the solution had been digested with sulphurous acid in order to reduce the arsenic acid.

The behaviour of tersulphide of arsenic was then examined.

One-tenth grn. of arsenious acid was precipitated as sulphide, the latter dissolved in hydrochloric acid and chlorate of potassa, and the solution evaporated on the water-bath till the odour of chlorine was no longer perceptible. One-half of this liquid ($= 0{\cdot}05$ grn. AsO_3) was introduced into the decomposing tube, but no indication of arsenic was obtained in 15 minutes.

The other half was saturated with sulphurous acid gas, digested for some time in the water-bath, and evaporated till the odour of sulphurous acid had disappeared. On subjecting it to the electrolytic test, a distinct mirror of arsenic was obtained in 10 minutes.

One-tenth grn. of tersulphide of arsenic ($= 0{\cdot}06$ grn. As) dissolved in diluted sulphide of ammonium was added to a mixture of articles of food similar to that previously used, with the addition of $\frac{1}{2}$ oz. of strong ale.

The mixture was digested on a water-bath with 1 oz. of hydrochloric acid and 3 oz. of water, chlorate of potassa being added in small quantities until a thin homogeneous fluid was obtained; the

filtered liquid was digested for half an hour with a large excess of a saturated solution of sulphurous acid, then evaporated on the water-bath to about $1\frac{1}{4}$ oz.

One half of this very nasty brown syrupy liquid was mixed with a drachm of alcohol and introduced into the decomposing cell. The want of mobility in the liquid somewhat retarded the evolution of gas, but in less than 15 minutes, the arsenical deposit commenced, and in 30 minutes, a very beautiful mirror was obtained.

In one or two of the experiments with organic mixtures, minute quantities of arsenic had escaped detection without any assignable cause; and I was therefore led to make some experiments to ascertain whether any influence was exerted by a variation in the amount of hydrochloric acid present in the solution.

A standard solution was prepared by dissolving 1 grn. of arsenious acid, in 1000 grns. (by measure) of hydrochloric acid.

10 grns. of this solution ($\frac{1}{100}$ grn. AsO_3), mixed with 20 grns. of hydrochloric acid, gave a very distinct crystalline deposit of arsenious acid in the tube, but no sublimate of metallic arsenic, although a deposit of arsenic was formed upon the negative plate. 100 grns. of the solution ($\frac{1}{10}$ grn. AsO_3) mixed with 200 grns. of hydrochloric acid, gave a similar result. 50 grns. of the solution ($\frac{1}{20}$ grn. AsO_3), diluted with 400 grns. of water, behaved in the same way.

In these cases, the arseniuretted hydrogen appeared to have been converted into terchloride of arsenic, which was decomposed by the aqueous vapour on passing the heated portion of the tube, with formation of arsenious acid.

Finding that, in these experiments, the smell of chlorine was distinctly perceptible at the end of the evolution tube, and believing that the chlorine disengaged at the positive plate, diffusing itself through the liquid, caused the decomposition of the arseniuretted hydrogen, I employed another apparatus, consisting of two decomposing cells, separated by a diaphragm of vegetable parchment.

In this form of apparatus, 10 grns. of the solution of arsenious acid in hydrochloric acid ($= \frac{1}{100}$ grn. AsO_3), mixed with 120 grns. of hydrochloric acid, and introduced into the negative cell of the apparatus (the latter having been charged, as usual, with a fluid ounce of dilute sulphuric acid), gave a beautiful mirror of arsenic in two minutes.

A mixture of articles of food, to which $\frac{1}{100}$ grn. of arsenious acid had been added, was digested with a fluid ounce of hydrochloric acid, and three or four ounces of water; the filtered solution was evaporated down to one ounce upon the water-bath, and one-tenth of it ($= \frac{1}{1000}$ grn. AsO_3), was introduced into the apparatus with $\frac{1}{2}$ drm. alcohol. In less than fifteen minutes, a very distinct arsenical mirror had been formed.

The apparatus which was ultimately found most suitable for the detection of arsenic by electrolysis, consisted of a two-ounce narrow-mouthed bottle, the bottom of which had been cut off, and replaced by a piece of vegetable parchment tightly stretched over it and secured by a ligature of thin platinum wire (even vulcanised caoutchouc is speedily corroded). The bottle was furnished with a cork, carrying a small tube, bent at right angles, and connected with the drawn-out reduction tube by a caoutchouc tube; through this cork passed a platinum wire bent into a hook, inside the bottle, for suspending the negative plate. The bottle was placed in a glass of such a size, as to leave a small interval between the two, and this glass was allowed to stand in a large vessel of cold water; an ounce of dilute sulphuric acid was introduced into the apparatus, so as to fill the bottle and the outer space to about the same level, the positive plate being immersed in the acid contained in this outer space. When the bottle had become filled with hydrogen, the shoulder of the reduction tube was heated to redness during fifteen minutes, to ascertain the purity of the sulphuric acid, and the liquid to be tested was introduced into the bottle, by means of a pipette, the cork being removed for an instant; a drachm of alcohol was afterwards introduced by the pipette to prevent frothing.

In the following cases, the arsenic was most satisfactorily detected in this apparatus, the evidence of its presence being threefold, and resting, firstly, upon the formation of the characteristic arsenical mirror; secondly, upon that of a small shining ring of crystalline arsenious acid, slightly in advance of the mirror; and thirdly, upon the development of the peculiar alliaceous odour.

$\frac{1}{1000}$ grn. arsenious acid in hydrochloric solution.
$\frac{1}{10000}$ " " aqueous solution.
$\frac{1}{100}$ " dissolved in 120 grns. hydrochloric acid.
$\frac{1}{200}$ " " 115 " "
$\frac{1}{1000}$ " " 120 " "
and 240 grns. water.

These experiments were repeated with the same results.

Experiments were then made upon organic mixtures containing arsenic, which were boiled with hydrochloric acid and chlorate of potassa, the arsenic acid being afterwards reduced to the arsenious, by digesting with sulphurous acid, or better with a few drops of a strong solution of bisulphite of soda.

By this process, $\frac{1}{100}$ grn., and even $\frac{1}{1000}$ grn. of arsenious acid, could be detected in an organic mixture with the greatest ease and certainty.

If the sulphurous acid be not entirely expelled after the reduction, a little tersulphide of arsenic is deposited in advance of the metallic crust.

The following process appeared to me the most trustworthy, for the detection of minute quantities of arsenic in articles of food.

The solid matters are reduced to a pretty fine state of division, mixed with enough water to form a thick gruel, and digested, in a a dish placed on a water-bath, with about $\frac{1}{2}$ oz. of hydrochloric acid, for an hour, powdered chlorate of potassa being occasionally added, as directed by Fresenius and von Babo, until the organic matters are disintegrated, when the liquid is filtered off, and evaporated to about an ounce upon the water-bath. The brown fluid thus obtained, is poured into a flask, and a few drops of a strong solution of bisulphite of soda are added to it, until it smells strongly of sulphurous acid; the flask is then heated in a water-bath, until this odour has disappeared, when the solution is mixed with at least an equal volume of water, and introduced into the apparatus arranged and charged as above, a little alcohol being poured upon the top. The operation should be continued for half an hour before the absence of arsenic is inferred.

The advantages which appear to me to belong to this mode of testing, are, that it involves the use of a metal which has never been known to contain arsenic; that the very same portion of sulphuric acid which is employed throughout may be subjected to the test for any length of time, before the suspected liquid is introduced; that the evolution of gas is uniform throughout the experiment, and is always so slow, that no dread of losing the arsenic need assail the mind of the operator; that the experiment may be interrupted for any length of time, by breaking the contact with the battery, without the least injury; that the foulest liquids can be as readily tested as those which are perfectly clear;

and that the same portion may afterwards be further tested by any other process.

The importance of this last consideration was fully exemplified in some of the early failures, before I was well acquainted with the test, for I always succeeded in detecting the arsenic in the same portion of the liquid by Marsh's test.

It is evident, moreover, that this operation enables us to detect minute quantities of copper, antimony, mercury and bismuth, if they be present in the solution.

On considering the detection of the other poisonous metals in this way, it is obvious that lead must be altogether excepted, on account of the insolubility of its sulphate. Silver must also be omitted, where hydrochloric acid is the solvent; and baryta, of course, would not be expected to answer. The remaining important poisonous metals, antimony, copper, mercury, bismuth and zinc, were therefore tried, bismuth being included, on account of the medicinal use of its compounds.

Detection of Antimony.

1 grn. of tartar-emetic (= 0·36 grn. Sb) dissolved in water, was introduced into the decomposing cell. A mirror of antimony was formed, just at each margin of the flame which heated the reduction tube, and a copious deposit of antimony was formed on the negative plate.

$\frac{1}{10}$ grn. of tartar-emetic (= 0·036 grn. Sb), gave only a slight white incrustation, and no mirror, in the reduction tube. The black deposit of antimony on the negative plate was dissolved by heating the latter with a few drops of yellow sulphide of ammonium; on decomposing this solution with acetic acid, a very distinct orange precipitate of tersulphide of antimony was obtained. A mixture of articles of food was mixed with $\frac{1}{10}$ grn. of tartar-emetic, and treated exactly according to the process above described for the detection of arsenic. There was no appearance of a metallic deposit in the reduction tube in twenty minutes; but there was a thick coating of antimony upon the negative plate, which was dissolved by yellow sulphide of ammonium. A portion of this solution, when evaporated in a watch-glass on the water-bath, left a residue having a decided orange colour.

A second and even a third coating of antimony was obtained,

by again immersing the plate for a few minutes, and when the film was very slight, it was at once identified by the orange stain produced, when a drop of sulphide of ammonium was evaporated upon it.

The result of the two last experiments, which was fully confirmed in all subsequent trials, is a very important one, as showing that minute quantities of antimony are not nearly so likely to be mistaken, even for a time, for arsenic, in the electrolytic, as in Marsh's test, and this seems attributable to the superior electro-positive tendency of antimony, which disposes it to precipitate more readily upon the negative plate. In no case have I failed to detect antimony in this way.

The following mode of proceeding may be recommended for the detection of the poisonous metals by electrolysis :—

The mixture, which may, of course, have been previously examined for organic poisons, by the usual methods, is digested, on a water-bath, with so much water, hydrochloric acid, and chlorate of potassa, as may be required to disintegrate the solid portions, and to render the liquid capable of filtration ; the filtrate is evaporated on the water-bath to a small bulk, and digested in a flask with a sufficient quantity of solution of bisulphite of soda to impart a strong odour of sulphurous acid. The solution is heated in the water-bath until the odour has disappeared, and is once more concentrated, if necessary, by evaporation. It is then diluted with a volume of water, equal to *at least* twice that of the hydrochloric acid present, and introduced into the decomposing cell, enough alcohol being poured upon it to prevent any inconvenient frothing. The passage of the current having been continued for about an hour, the negative plate is withdrawn, washed, and boiled in somewhat dilute yellow sulphide of ammonium for a minute or two. This solution is then evaporated in a watch-glass, placed on the water-bath, and the orange residue of sulphide of antimony identified by the usual tests. The platinum plate having been again washed, is boiled in a few drops of concentrated nitric acid, to which a drop of dilute hydrochloric acid should be added, to dissolve the sulphide of mercury. The acid solution is boiled down in the test tube to a small bulk, and mixed with an excess of ammonia, when the presence of copper will be rendered evident, and the teroxide of bismuth will be precipitated, together with a little ammonio-chloride of platinum. This precipitate when

dissolved in hydrochloric acid, evaporated, and largely diluted, will present the indication of bismuth. The filtered ammoniacal liquid, acidulated with hydrochloric acid, and boiled with clean copper, affords the usual evidence of the presence of mercury.

Of the metals above mentioned, mercury was found to be the only one which interferes with the detection of arsenic.

If this metal be detected, the liquid taken from the decomposing cell (or a fresh portion of the original hydrochloric solution), may be distilled, according to Dr. Odling's recommendation, in order to separate the arsenic from the mercury.

The residue may still, if the analyst deem it expedient, be further dealt with by incineration or otherwise, for the detection of other metals.

V.—*On the Composition of Air from Mont Blanc.*

By Dr. E. Frankland, F.R.S.

The greatly increased perfection of gasometric analysis and the numerous minute investigations made by Regnault, Bunsen and others during the past ten or fifteen years, have rendered our knowledge of the composition of atmospheric air exceedingly complete, as far at least as its two chief constituents are concerned. The earliest analyses of air led chemists to believe that the relative proportions of these constituents were liable to very considerable fluctuations. As the processes employed, however, became more accurate, these discrepancies gradually disappeared; until, at length, carefully conducted experiments showed an apparent uniformity in the composition of samples of air taken from the most widely different localities; but it remained for subsequent and far more delicate methods of research to demonstrate that, notwithstanding these apparently accordant results, the composition of the atmosphere does in reality exhibit certain fluctuations, confined, however, within very narrow limits.

The first series of experiments belonging to the latter category, and which may be said to have first established the variability of the percentage of atmospheric oxygen, are those of Bunsen, made

upon samples of air collected at Marburg on ten different days, and exhibiting, when freed from carbonic acid, a percentage of oxygen varying from 20·973 to 20·840, whilst no two analyses of the same sample differed more than ·031 per cent. from each other.

Then followed a most elaborate series of determinations by Regnault, begun in December, 1847, upon the air of Paris, and continued in January, 1848. The variations in the percentage of oxygen here observed were, in December, 1847, from 20·90 to 21·00, and in January, 1848, from 20·89 to 20·99.

Lewy collected air near the surface of the sea, on the 18th December, 1847, at 3 P.M., in lat. 21° 9′ N. and long. 12° 52′ W. of Paris, temperature 21° C. and found it to contain :—

Nitrogen . . .	78·886
Oxygen . . .	21·060
Carbonic Acid . .	·054
	100·000

Another specimen collected December 4th, 1847, at 3 A.M. in lat. 47° N. and long. 13° W., temperature 13° C. contained :—

Nitrogen . . .	79·006
Oxygen . . .	20·961
Carbonic Acid . .	·033
	100·000

A large number of analyses by the same chemist demonstrate that the air near the surface of the sea contains about the same proportion of carbonic acid as that resting upon the land, and that the sea air is richer, both in oxygen and carbonic acid by day than by night; a fact which he explains by assuming that dissolved air is liberated during the day from the heated surface-layer of the ocean, such dissolved air being, as is well-known, much richer than atmospheric air in the two gases just named. Lewy also made a very extended series of analyses of air collected at New Granada and Bogota, during the dry and rainy seasons. The mean of eleven analyses of air from New Granada gave :—

Nitrogen . . .	78·946
Oxygen . . .	21·014
Carbonic Acid . .	·040
	100·000

Analyses of air from Bogota collected during the dry and rainy seasons gave the following mean numbers:—

	Dry Season.	Rainy Season.
Nitrogen . .	78·932	78·966
Oxygen. . .	21·022	20·996
Carbonic Acid .	·046	·038
	100·000	100·000

On some occasions, the air of New Grenada was found to contain as much as 0·49 per cent. of carbonic acid, on which occasions the percentage of oxygen fell as low as 20·331. This abnormal composition is ascribed to volcanic eruptions and extensive conflagrations. In nearly all cases, Lewy seems to have found that an increased amount of carbonic acid in the air was accompanied by an increase in the percentage of oxygen.

Messrs. H. and A. Schlagintweit determined, by weighing, the amount of carbonic acid in the air at great elevations in the Eastern Alps by absorption with potash; but as the increase in weight of the potash apparatus was only from 3 to 6 milligrammes in each experiment, and as the two weighings were made at intervals of nearly two months, these determinations can only be regarded as approximative. Messrs. Schlagintweit found the volume of carbonic acid to vary from ·032 to ·058 per cent. Up to an altitude of 11,043 feet, they found a gradual increase of carbonic acid, but at this elevation they conceived that a constant maximum was arrived at. In some later experiments on the air of Monte Rosa, at heights varying from 13,374 to 13,858 feet, the same experimenters found a mean percentage of carbonic acid equal to ·079 and a maximum of ·095.

In the year 1852, M. Regnault published an extensive series of determinations of the percentage of oxygen in samples of air,

deprived of carbonic acid, from different localities. The following is a condensed summary of his results:

		Percentage of Oxygen.	
100 specimens	from Paris and neighbourhood (1848	20·913	20·999
9 ,,	,, Lyons, Montpelier & St. Martin-aux-Arbres .	20·918	20·966
30 ,,	,, Berlin (1848 & 1849) .	20·908	20·998
10 ,,	,, Madrid (1848) . .	20·916	20·982
23 ,,	,, Geneva, Mont Saléve and Mont Buet . . .	20·909	20·993
15 ,,	,, Toulon, the Mediterranean and Algiers .	20·912	20·982
5 ,,	taken during a voyage from Liverpool to Vera-Cruz .	20·918	20·965
1 ,,	from Guallalamba, South America	20·960	
2 ,,	,, the summit of Pichincha (15,924 feet) . .	20·949	20·988

In this investigation, a few remarkable deviations from these normal amounts of oxygen were observed, viz.:—

	Percentage of Oxygen.	
Air collected in the Harbour of Algiers, June 5th, 1851	20·42	20·395
Air from Bay of Bengal, February 1st, 1849 .	20·46	20·45
Air from Ganges, March 8th, 1849. Temperature 35° C., foggy weather, much decomposing organic matter in the water. Commencement of an outbreak of cholera . .	20·390	20·387

It would be interesting to know how far these results were really abnormal, as regards the relative proportions of oxygen and nitrogen, since it is not improbable that the apparently small percentage of oxygen indicated, was in reality due to the presence of gaseous organic matters in larger quantity than usual; the ignition of these with excess of hydrogen, in the mode adopted in these analyses would have the effect of converting the carbon of such organic matters into carbonic oxide, thus diminishing the contraction of volume on explosion and consequently the apparent

percentage of oxygen. Should such abnormal specimens of air be again encountered, it would be desirable, subsequently to the analysis made in the usual manner, to ignite other portions of them with an equal volume of mixed electrolytic gases, so as to convert the carbon of any organic matter that might be present into carbonic acid which could then be estimated in the usual manner by absorption with potash.

Dr. Miller examined air collected during a balloon ascent in August, 1852, at a height of 18,000 feet, and also a sample collected near the surface of the earth at the same time, with the following results:

	Air from altitude of 18,000 feet.	Air near the earth.
Percentage of Oxygen . .	20·88	20·92

After these numerous and minute analyses, establishing as they do, with few exceptions, the slight, but still undoubted, variations in the relative proportions of the two chief atmospheric gases, any further contributions to this particular branch of our knowledge can only be of comparatively small value. Nevertheless, as an opportunity was afforded me for collecting specimens of air whilst accompanying Dr. Tyndall, during the past summer, in his ascent of Mont Blanc for the establishment of thermometric stations, I did not regard a few further experiments upon air from great altitudes as entirely superfluous; since the discovery of the causes determining the variations in the composition of the atmosphere will probably only be arrived at by the accumulation of vast numbers of observations made at various points at and above the earth's surface. It will also be perceived, on reference to the various analytical results above given, that, with the exception of M. Lewy, no experimenter has made contemporaneous determinations of the three chief gaseous constituents of the air; and I was therefore anxious, if possible, to render these samples available for the determination of carbonic acid, as well as of the two other chief gases.

The very minute changes of volume, which the instrument I use for gaseous analysis is capable of registering, led me to hope that it might not be impossible to make direct determinations of carbonic acid in the few cubic inches of air which are usually sealed up for analysis; and a number of estimations of the carbonic acid in air, collected at St. Bartholomew's Hospital, proved that

this gas can be thus estimated, by absorption with caustic potash. Such an amount of air was taken for each determination, as was capable of supporting a column of mercury, from 600 to 800 millimeters high, which rendered any diminution of volume, to the extent of about $\frac{1}{7000}$ part, distinctly appreciable. The following results were obtained, those on the 26th of January, being seven successive determinations, extending over about three hours:

Date.	Percentage of Carbonic Acid.
Dec. 7, 1859	·042
Jan. 10, 1860	·064
" "	·077
26, "	·098
" "	·087
" "	·098
" "	·085
" "	·098
" "	·110
" "	·101

Although it cannot be doubted that there are other methods by which carbonic acid can be more minutely and accurately determined, whenever they can be carried out with the usual conveniences of a laboratory at hand, yet it is very questionable, whether any of these processes can rival this purely eudiometrical one, in cases where the operations have to be performed in the midst of all the inconveniences attending an experimenter at great altitudes. Any such estimations, involving the weighing of potash tubes at intervals of several days, or even weeks, are obviously not worthy of implicit confidence. In the above mode of determination, the actual change of volume, self-corrected for temperature, aqueous vapour, &c., being actually observed by the operator, an error exceeding ·01 per cent., is probably rarely or never committed.

In the following analyses of air from Mont Blanc, the carbonic acid was absorbed by a single drop of concentrated solution of caustic potash, and the oxygen was then determined by exploding the residual gas with excess of electrolytically prepared hydrogen.

Specimen collected at the Grands Mulets (altitude 11,000 feet), August 20th, 1859, at 6·45 P.M Wind, north, hail falling, but a moderately clear sky.

Estimation of Carbonic Acid.

I.

	Obs. vol.	Temperature C.
Air used	539·5	5·0°
After absorption of carbonic acid .	538·9	5·0°

Estimations of Oxygen.

II.

	Obs. vol.	Temperature C.
Air used	290·8	5·2°
After admission of hydrogen . .	486·5	5·2°
After explosion	304·9	5·2°

III.

	Obs. vol.	Temperature C.
Air used	248·7	5·2°
After admission of hydrogen . .	443·8	5·2°
After explosion	288·7	5·2°

Percentage Composition.

	I.	II.	III.	Mean.
Nitrogen .	..	79·096	79·124	79·110
Oxygen .	..	20·793	20·765	20·779
Carbonic acid	0·111	..	..	·111
				100·000

Specimen taken at the summit (altitude 15,732 feet), August 21st, at 8·45 A.M. Wind, north; weather bright and sunny; air filled with particles of snow whirled up by the wind.

Estimation of Carbonic Acid.

I.

	Obs. vol.	Temperature C.
Air used	326·1	5·2°
After absorption of carbonic acid .	325·9	5·2°

Estimations of Oxygen.

II.

	Obs. vol.	Temperature C.
Air used	166·8	5·3°
After admission with hydrogen .	273·0	5·3°
After explosion	168·1	5·3°

III.

	Obs. vol.	Temperature C.
Air used	159·9	5·3°
After admission of hydrogen . .	302·7	5·3°
After explosion	202·7	5·3°

Percentage Composition.

	I.	II.	III.	Mean.
Nitrogen .	..	78·989	78·988	78·989
Oxygen .	..	20·950	20·951	20·950
Carbonic acid	0·061	..	..	·061
				100·000

Specimen collected at Chamonix (altitude 3000 feet), August 23rd, at 2 P.M. Wind north; sky clear.

Estimation of Carbonic Acid.

I.

	Obs. vol.	Temperature C.
Air used	474·1	5·4°
After absorption of carbonic acid .	473·8	5·4°

Estimations of Oxygen.

II.

	Obs. vol.	Temperature C.
Air used	255·6	5·0°
After admission of hydrogen . .	455·8	5·0°
After explosion	295·5	5·0°

III.

	Obs. vol.	Temperature C.
Air used	217·4	5·0°
After admission of hydrogen . .	377·3	5·0°
After explosion	241·1	5·0°

Percentage of Composition.

	I.	II.	III.	Mean.
Nitrogen .	..	79·045	79·067	79·056
Oxygen .	..	20·892	20·870	20·881
Carbonic acid	·063	..	..	·063
				100·000

So far as the nitrogen and oxygen are concerned, the composition of these samples of air falls within the limits of variation noticed by former experimenters; but, although the comparatively high percentage of carbonic acid, at the Grands Mulets, confirms the observations of the Messrs. Schlagintweit, as to the presence of a larger amount of this gas at great elevations, yet the diminution of the quantity to about the normal amount upon the summit, shows, either that this gas attains a maximum at a height of about 11,000 feet, and again diminishes above this altitude, or, as is much more probable, the percentage of carbonic acid is *generally, but not invariably*, greater in the higher regions of the atmosphere. These results also exhibit a correlation between atmospheric oxygen and carbonic acid, for when the one increases the other diminishes,—a fact which will be better seen from the following comparison:—

	Percentage of carbonic acid.	Mean percentage of oxygen, in air free from carbonic acid.
Grands Mulets . .	·111	20·802
Summit . . .	·061	20·963
Chamounix . . .	·063	20·894

This result, if it be confirmed, cannot be regarded as altogether unexpected, when we consider the effects of vegetation, combustion, and respiration upon the constituents of the atmosphere; but both this and the comparative amount of carbonic acid at great altitudes, are problems, the solution of which must be left to future and more extended inquiries.

VI.—*On Refining Gold when alloyed with Tin or Antimony, so as to render it fit for the purposes of Coinage.*

By Robert Warington.

Towards the latter end of the year 1857, I received from the Australian Bank, a specimen of bar-gold for analysis, which was stated to have been obtained from the quartz-crushing process. On the exterior, or what had been the surfaces of the original bar, it presented the general appearance of a golden hue, though perhaps, an experienced and critical eye, might have considered it a little paler than pure gold. Interiorly, or on the broken surface, however, it had a crystalline structure of a greyish yellow colour. It was very brittle and rotten, and by analysis, yielded the following results on the 100 parts.

Gold	92·50		
Silver	4·60		
Tin	2·00	with a trace of antimony	
Copper	0·75		
	99·75		
Loss	0·25		
			100·00

I have been informed that numerous bars of this white and brittle gold, had arrived in this country from Australia, and had caused much trouble and annoyance to the refiners, melters, and also to the Mint officers, as it will be evident, that the nature of the alloying metals is not rendered apparent in the ordinary mode of assay, by the processes of cupellation and quartation, they being oxidized, dissolved, and carried into the cupel with the lead; and that therefore, in the after larger operations of melting, when the gold passes forward for the purposes of coinage, the existence of the tin and antimony not having been discovered, is not provided for, and consequently, from the brittle nature of the alloy, the subsequent processes of rolling, to which it has to be subjected, are rendered impracticable. I am informed that about 17,000 ounces of gold bars have in this condition been returned to the Bank of England authorities from the Mint, as unfitted for the purposes of coinage.

A short time after the foregoing examination was completed and reported on, I received another specimen of this brittle gold for analysis, through other parties. This second sample presented somewhat the same appearances, both externally and internally, as the one just described, being perhaps, a little whiter in its colour, and more rotten or friable in texture. It yielded by analysis, on the 100 parts:—

Gold	93·80	
Silver	2·20	
Antimony	2·28	
Tin	1·40	
Arsenic, Copper	traces	
	99·68	
Loss	0·32	
		100

An interesting question arises from the above results as to the origin of these injurious alloying metals; do they occur associated with the gold, or are they introduced during the melting process? As regards the first, we know that in stream works, gold and oxide of tin are commonly found associated, as is the case in Ceylon, in Cornwall, and other districts. We know also, that considerable quantities of stream-tin are brought from Australia. The presence, therefore, of that metal in small quantities, as an alloy, in the resulting gold bars, might be almost anticipated. But this view of the case does not account satisfactorily, for the other alloying metals found in the second analysis, particularly the antimony. My own impression, derived from a careful examination of the specimens and the foregoing results, is, that they are introduced during a rough process of refining, through the employment of sulphuret of antimony, and that, for want of efficient management, the operation has been imperfectly carried out.

The use of sulphuret of antimony, for the purpose of refining gold and raising its standard, is so well known, that I need hardly dilate upon it; suffice it to say, that, if successfully applied, it converts the iron, zinc, tin, &c., that may be present, and much of the silver, into the form of sulphurets, which float, in their melted state, upon the surface of the gold; a portion of the antimony at the same time alloying with that metal. This antimony should, of course, be afterwards removed by a second

operation.* From a specimen which has since come into my possession, it will be seen that the particles of gold dust have been so imperfectly melted, before running into bars, that many of them are still visible in their flattened and rounded forms, and must therefore have remained suspended in the melted alloy. I feel that this explanation of the source of the alloying metals is, therefore, to some extent substantiated, as a want of a sufficiently high and continued heat would leave the gold very much in the state above described.

On delivering the report of this second analysis to the parties from whom I had received the sample, they were anxious to know if I could suggest to them a method by which these injurious alloys could be removed, and the gold rendered capable of being rolled or hammered, without, at the same time, greatly increasing the expense of the operations, or entailing a loss of the gold. I was in consequence induced to turn my attention to the effecting of this desirable object. The proper resolution of this problem required a little consideration, inasmuch, as, although it was evident that it must be accomplished by a process of oxidation, to burn out, as it were, the antimony and tin; yet it was also necessary that the oxygen should be applied to the alloyed gold while the metal was in its fluid state, and also that the oxidizing agent should not part with its oxygen simply by the high temperature to which it would be subjected.

Nitrate of potash I was informed had been suggested, tried and failed, although a very large percentage had been used; experiments in that direction were therefore considered unavailable, and my attention was consequently turned to the employment of metallic oxides having a weaker affinity for oxygen, at these high temperatures, than the metals which it was required to remove from the contaminated gold.

After a few experiments, all of which were more or less successful, I succeeded in obtaining the desired result, and submitted for the consideration of the parties concerned, a simple process, which, from their liberality, I was enabled at the time to communicate to several friends interested in such matters, and which I also desire now to lay before the members of the Chemical Society. The process consists in the employment of oxide of copper, about 10 per cent. of which is to be added

* Since making this communication, I have been informed that sulphate of antimony also sometimes occurs in association with native gold in Australia.

to the alloyed gold, with the addition of a small quantity of borax, and the whole maintained in a well fused state for about half an hour. The result is a perfectly malleable gold containing a small percentage of metallic copper, and well fitted for the purposes of coinage. The proportion of oxide of copper used must of course greatly depend on the percentage quantity of the oxidable metal requiring to be removed; but I believe, from the specimens which I have worked on, that it never need exceed the 10 per cent. Oxide of manganese might be employed to effect the same purpose; but I found that the fusibility of the oxide of copper and its powerful fluxing properties, rendered its action much more efficient and complete, from its flowing continually over the surface of the molten gold, and thus thoroughly oxidizing and removing the tin and antimony from their combination. As thus conducted the resulting alloy should always be better than standard, unless the baser metals occur in very large proportion.

By the action of nitro-hydrochloric acid upon these samples of alloyed gold, the resulting solution deposited on cooling beautiful crystals of chloride of silver; and I may be allowed here to mention a very curious case of the same kind, but to a much greater extent, which was brought under my notice some time since, by the late Mr. Maurice Scanlan. It appeared from his statement, that he had been requested to obtain the gold from a beautifully wrought and small sized rope-chain, of Indian manufacture; and on submitting it to the action of nitro-hydrochloric acid for this purpose, he found that it did not dissolve; and although he obtained some gold in solution, yet the form and size of the delicate fabric remained unaltered; it had become, however, very brittle and rotten, and was of a dingy brown colour. It was submitted to me for examination by the microscope, and when subjected to this scrutinizing agent, it was at once evident what had taken place, and of what the chain had been composed. It consisted almost entirely of chloride of silver, beautifully crystallised on the surface or strands of the rope, and having, in the cross section, a radiating structure from the interior to the circumference, the central core, in some fragments, exhibiting still a portion of the original alloy from which the gold had not been removed, it having, most probably, been protected from the action of the acid by the comparatively thick coating of chloride of silver which had been formed around it.

VI.—*On some Derivatives from the Olefines.*

By Frederick Guthrie.

II.

The terms *isotype* and *idiotype*, *isotypic* and *idiotypic* may be advantageously adopted to denote bodies which belong to similar types, or to the same one, and the relations which such bodies bear to one another. The application of these expressions, which are almost self-explicatory, is best seen in examples.

A body is idiotypic with all its replacement derivatives; the latter are, of course, idiotypic with one another; the whole are idiotypes.

Bodies belonging to the same chemical series are isotypic with one another or are isotypes. Hence

(1.) The idiotypes of the same body are idiotypes of one another.

(2.) The isotypes of the same body are isotypes of one another.

(3.) The idiotypes of the same body are isotypes of the idiotypes of an isotypic body.

(4.) The isotypes of the same body are isotypes of the idiotypes of an idiotypic or isotypic body.

In a paper read before the Chemical Society (March 3rd, 1859,) I described the formation and some of the properties of the bodies $C_4H_4Cl_2S_2$, $C_{10}H_{10}Cl_2S_2$, $C_{10}H_{10}ClS_2$ and of some derivatives obtained from them. I purpose now resuming the consideration of this interesting class of bodies obtained by the action of the two chlorides of sulphur upon the olefines, and rendering their history somewhat more complete, before discussing the behaviour of the other compound halogens towards the same hydrocarbons.

In the paper referred to, it was asserted that bisulphide of chlorine is without action upon ethylene at temperatures between 0° and 100° C. The hope was, however, expressed that the two might combine directly, as is the case with amylene, if they were subjected to increased pressure. I have since found that even at ordinary pressures, an increased temperature is sufficient to determine chemical recomposition; and from analogies, afterwards to be pointed out, I conclude that the most probable interpretation of

such recomposition is the direct union of the two reagents, ethylene and bisulphide of chlorine, and the simultaneous decomposition of the product formed.

Action of bisulphide of chlorine upon ethylene.—Three or four ounces of bisulphide of chlorine are brought into a retort of two or three pounds capacity. The retort is connected with an inverted condenser, and through a tube, passing through the tubulus into the bisulphide, a rapid current of pure dry ethylene is allowed to pass. On heating the bisulphide to ebullition, the two substances are brought together in a gaseous state at a temperature of about 139° C.; a condition which appears greatly to promote their reaction. After about 200 litres of ethylene have passed through, the liquid which has deepened in colour, is transferred to a smaller retort and heated till the boiling point rises to 180° C. During this distillation, as well as during the passage of the ethylene, a disengagement of hydrochloric acid takes place. On allowing the residue in the retort to cool, a considerable quantity of sulphur separates out. The distillate, which contains only a small quantity of substance undecomposible by water, may be employed in subsequent operations. In order to free the organic compound in the unvolatilized residue from still adhering bisulphide of chlorine, it is, after separation from the sulphur, digested for many hours with water at 80°. After fresh portions of water no longer become acid, the residue, which is pasty and opaque, is allowed to stand for two or three days in contact with dilute caustic soda. After drying, it is digested with ether, and the same process of purification followed, which has been frequently described in my former paper.

In burning this substance with oxide of copper, it was weighed in an open boat and chlorate of potash was employed. This same method was used with the non-volatile bodies afterwards to be described. In the determination of the sulphur of this and other bodies, I have employed carbonate of zinc in conjunction with chlorate of potash, instead of the carbonates of soda or magnesia; the first of these attacks the glass, and the subsequent separation of silicic acid renders the filtration troublesome; the second is so light as to be prone to projection from the tube; and both are difficult to procure free from sulphuric acid. The carbonate of zinc prepared from the chloride, or the oxide of zinc prepared by the combustion of zinc, may, I think, in all cases advantageously

replace the before-mentioned carbonates for sulphur determinations. The zinc may also be used in union with oxide of mercury in Russell's method. In all cases, however, the combustion tube should be about 20 inches long and the anterior eight inches should be kept cold.

I. 0·4637 grm. gave 0·3199 grm. carbonic acid and 0·0980 grm. water.

II. 0·2286 grm. gave 0·0445 grm. water.

III. 0·3960 grm. gave 0·2747 grm. carbonic acid and 0·0735 grm. water.

IV. 0·2564 grm. gave 0·4559 grm. sulphate of baryta.

V. 0·2876 grm. gave 0·6178 grm. chloride of silver.

Calculated.		Found.					
		I.	II.	III.	IV.	V.	Mean.
C_4 . .	18·45	18·81	,,	18·92	,,	,,	18·86
H_3 . .	2·31	2·33	2·12	2·06	,,	,,	2·17
S_2 . .	24·61	,,	,,	,,	24·35	,,	24·35
Cl_2 . .	54·62	,,	,,	,,	,,	53·14	53·14
	99·99						98·52

The substance analysed has accordingly the composition $C_4H_3S_2Cl_2$ having been formed according to the equation—

$$C_4H_4 + 3S_2Cl = C_4H_3S_2Cl_2 + HCl + 4S$$

which also explains the liberation of hydrochloric acid and the separation of free sulphur, described in the preparation of the body. Probably the most appropriate name for this body would be the *bisulphochloride of chlorethylene,* its formula being

$$C_4\left\{\begin{matrix}H_3\\Cl\end{matrix}\right\}S_2Cl$$

inasmuch as in all likelihood, one atom of hydrogen has been replaced by one of chlorine, and the so-formed chlorethylene has combined with the bisulphide of chlorine; or the bisulphide of chlorine has combined with the ethylene to $C_4H_4S_2Cl$, and this body has decomposed two more atoms of bisulphide of chlorine, forming hydrochloric acid and bisulphochloride of chlorethylene:

$$C_4H_4S_2Cl + 2S_2Cl = C_4\left\{\begin{matrix}H_3\\Cl\end{matrix}\right\}S_2Cl + 4S + HCl$$

It is clear however that it may be viewed also, either as the bichlorosulphide of vinyl,

$$C_4H_3S_2Cl_2$$

which would however be without analogues, or as the bisulphide of bichlorethyl,

$$C_4 \left\{ \begin{matrix} H_3 \\ Cl_2 \end{matrix} \right\} S_2.$$

Bisulphochloride of chlorethylene is a transparent liquid of light yellow colour. Its taste is sweet and pungent. Its smell when fresh is agreeable, being between those of peppermint and of oil of lemons. Three or four drops when swallowed produce headache. It is soluble in ether and alcohol, insoluble in water; it does not volatilize without decomposition. At 11° C. its specific gravity is 1·599.

It is worthy of note that the bichlorosulphide of ethylene $C_4H_4S_2Cl_2$ obtained by the direct union of chloride of sulphur with ethylene and described in the former paper, differs from the body just described only in having one more atom of hydrogen, a difference which might not appear on analysis. The specific gravity of the latter body however is only 1·408, its smell is quite distinct, and it is much less soluble in ether.

The determination of the composition of bisulphochloride of chlorethylene suggested three questions:—

(1.) Is its formation preceded by that of the bisulphochloride of ethylene $C_4H_4S_2Cl$, which undergoes decomposition on heating in presence of two additional molecules of S_2Cl?

(2.) May it be regarded as a substitution-product of bisulphide of ethyl, being in fact the bisulphide of bichlorethyl $C_4 \left\{ \begin{matrix} H_3 \\ Cl_2 \end{matrix} \right\} S_2$?

(3.) Does it admit of further exchange of hydrogen for chlorine, whether such chlorine replacement-products be identical or not with the hitherto hypothetical chlorine substitution-products of bisuphide of ethyl.*?

* Ann. Ch. Phys., [3], xviii. Cahours mentions that chlorine acts upon the bisulphide of ethyl; but the products do not appear to have been examined.

The question (1) may be answered approximately by submitting the bisulphochloride of amylene $C_{10}H_{10}S_2Cl$, described in the former paper to the action of two additional molecules of bisulphide of chlorine at a high temperature.

Question (2) must be answered by submitting bisulphide of ethyl to chlorine.

To answer question (3) bisulphochloride of chlorethylene must be acted on by chlorine.

On passing dry chlorine into bisulphochloride of chlorethylene, a rapid disengagement of hydrochloric acid results, accompanied by a liberation of heat which, under favourable circumstances, may raise the temperature of the liquid from 12° C. to 85° C.; at the same time the liquid loses almost all its colour. In the following experiments the reaction was carried on in the dark.

Through eight or ten grammes of bisulphochloride of chlorethylene, dry chlorine was passed, until the heat at first developed had abated, and the ordinary temperature was re-established. The tube containing the product was then heated in a water-bath to 100° C., and a rapid current of dry chlorine was passed through for two hours. The product was freed from dissolved hydrochloric acid and chlorine by being again heated to 100° C. and subjected to a rapid current of dry carbonic acid for two hours. Even after all the hydrochloric acid was expelled, the carbonic acid, in passing through the liquid at 100° C. continued to carry off a vapour which both fumed with ammonia and reddened litmus paper. This is due to the vapours of chloride of sulphur and oxychloride of sulphur as we shall presently see.

The cold gas-exit-tube became coated with a layer of yellowish transparent crystals, too small in quantity for examination, and consisting probably of oxychloride of sulphur, whose formation was due to a trace of moisture. After the carbonic acid had passed through during the time mentioned, a drop of the liquid did not give up any hydrochloric acid to water. It was, however, digested with warm water, dissolved in ether, then dried and purified as before.

On analysis this body showed the following composition :—

	grm.		grm.		grm.	
I.	0·3737	gave	0·2182	carbonic acid and	0·0374	water.
II.	0·5184	„	0·4116	sulphate of baryta.		
III.	0·4453	„	1·2957	chloride of silver.		

	Calculated.	Found. I.	II.	III.	
C_4 . .	16·16	15·94	,,	,,	
H_2 . .	1·35	1·11	,,	,,	
S . .	10·76	,,	10·88	,,	
Cl_3 . .	71·73	,,	,,	71·98	
	100·00				99·91

The action of chlorine, therefore, under these circumstances upon the bisulphochloride of chlorethylen is to replace one atom of hydrogen by chlorine and to eliminate half the sulphur; thus giving rise to a body which may be called the *chlorosulphide of bichlorethylene.*

$$C_4 \left\{ \begin{matrix} H_2 \\ Cl_2 \end{matrix} \right\} SCl.$$

The reaction takes place according to the equation

$$C_4H_3Cl_2S_2 \ + \ 3Cl \ = \ C_4H_2Cl_3S \ + \ HCl \ + \ 3Cl$$

The chlorosulphide of bichlorethylene is a yellowish, almost colourless, transparent liquid of pungent, suffocating, and most persistent smell. It mixes with ether and alcohol, but is insoluble in water. Although not volatile when heated alone, it may be volatilized almost without residue in a current of dry carbonic acid. Its specific gravity is 1·225 at 13·5° C.

In order to compare the products of the action of chlorine upon bisulphide of ethyl with those of its action upon the bisulphochloride of chlorethylene, ten or twelve grammes of the bisulphide of ethyl were exposed to the action of chlorine in the same apparatus, and as nearly as possible under the same physical conditions as obtained during the action of chlorine upon the bisulphochloride of chlorethylene.

On passing a rapid current of dry chlorine into the above quantity of bisulphide of ethyl, the temperature was raised from 14° to 78° C., abundance of hydrochloric acid being evolved. The first bubbles of chlorine, passed through the liquid, became opalescent, owing to the separation of sulphur. As, however, the temperature rose, this opalescence speedily disappeared. At one stage, the liquid became much darker in colour than the sulphide

of ethyl; subsequently it regained its light straw-colour; when this happened, the evolution of heat ceased. The liquid product so formed was thereon heated to 100° C. in a water-bath, and the current of chlorine continued for two hours; it was then freed from hydrochloric acid and chlorine by a stream of carbonic acid, as described in the preparation of the chlorosulphide of bichlorethylene.

A product was thus obtained, having the same colour and precisely the same exceedingly characteristic smell as the chlorosulphide of bichlorethylene, formed, as already described, by the action of chlorine upon the bisulphochloride of chlorethylene. Its specific gravity was found to be 1·219 at 13·5° C., which is identical with that of the chlorosulphide of bichlorethylene.* Analysis also showed the two to contain the elements carbon, hydrogen, sulphur, and chlorine in the same proportions as they exist in the chlorosulphide of bichlorethylene.

I. 0·3623 grm. gave 0·2177 grm. carbonic acid and 0·0329 grm. water.

II. 0·4073 grm. gave 0·4113 grm. sulphate of baryta.

III. 0·2762 grm. gave 0·7702 grm. chloride of silver.

	Calculated.	Found. I.	II.	III.	
C_4	16·16	16·38	,,	,,	
H_2	1·35	1·00	,,	,,	
S	10·76	,,	11·10	,,	
Cl_3	71·73	,,	,,	69·00	
	100·00				97·48

This liquid has therefore the formula:—

$$C_4 \left\{ \begin{matrix} H_2 \\ Cl_3 \end{matrix} \right\} S,$$

having been formed according to the equation:—

$$C_4H_5S_2 + 7Cl = C_4 \left\{ \begin{matrix} H_2 \\ Cl_3 \end{matrix} \right\} S + SCl + 3HCl,$$

and being, in accordance with its derivation, the *sulphide of terchlorethyl*.

* For exact comparison, the specific gravities of the two substances were taken in the same vessel and nearly at the same time.

I can detect no difference whatever between the substance just described, and that whose analysis was given on page 40, and named the chlorosulphide of bichlorethylene. The empirical formulæ of the two are identical, $C_4H_2Cl_3S$; but, if we insist upon evidencing the different sources of the two bodies in their formulæ and names, we must write the one:—

Chlorosulphide of bichlorethylene . $C_4 \left\{ \begin{matrix} H_2 \\ Cl_2 \end{matrix} \right\} SCl$, the other

Sulphide of terchlorethyl . . . $C_4 \left\{ \begin{matrix} H_2 \\ Cl_3 \end{matrix} \right\} S$.

That these two bodies are identical I believe no one who has had them in his hands will doubt. I must reserve the confirmatory evidence resulting from the apparent identity of some oxygen derivatives obtained in the same manner from both, for another occasion. But from the above facts alone we are perhaps justified in giving an affirmative answer to the question (2) above proposed; that is, we may look upon bisulphochloride of chlorethylene in its behaviour towards chlorine as a chlorine-substitution-product of bisulphide of ethyl. That we do not obtain the bisulphochloride of chlorethylene by acting upon bisulphide of ethyl with chlorine, is accounted for by the fact already proved, that the bisulphochloride of chlorethylene is itself attacked by chlorine. It is highly probable, however, that the darkening of the liquid, mentioned above, at one stage of the action of chlorine upon the bisulphide of ethyl, is owing to the formation of the bisulphochloride of chlorethylene, which subsequently undergoes further hydrogen-replacement and elimination of sulphur, being converted into the chlorosulphide of bichlorethylene. I did not, however, seek to intercept the process at this point, because no criterion could be formed of the integral nature of the action, and because even if a body of the anticipated composition had been formed, it might still have been a mixture of the higher substitution-product with the original substance.

The identity of the chlorine-substitution-products of $\left\{ C_4 \begin{matrix} H_3 \\ Cl \end{matrix} \right\} S_2Cl$ and $C_4H_5S_2$ is further of considerable interest, inasmuch as it shows that towards chlorine the two are essentially idiotypic, and that consequently, while we have seen, in the case of amylene, that a body, $C_nH_nS_2Cl$, acts towards oxides and hydrated oxides as the

chloride of a *sulphur*-radicle; towards chlorine such a body acts as the *sulphide* of a *chlorine*-radicle. This line of evidence will be more complete after studying the action of chlorine upon the bisulphochloride of amylene previously described.

If a rapid current of dry chlorine be passed through bisulphochloride of amylene, $C_{10}H_{10}S_2Cl$, hydrochloric acid is evolved. In order to compare this reaction with the action of chlorine upon bisulphide of ethyl and bisulphochloride of chlorethylene, ten or twelve grammes of the bisulphochloride of amylene were brought into the same apparatus and subjected to the action of chlorine, under the same circumstances as attended the action of that element upon the bodies mentioned. The action was attended by an evolution of heat which raised the liquid from 12° to 70° C. The colour changed from a light straw-yellow to a garnet-red at this point I suppose the liquid to consist principally of an intermediate substitution-product $C_{10}\left\{\begin{matrix}H_9\\Cl\end{matrix}\right\}S_2Cl$, and then became almost of its original paleness. At this point no more heat was evolved. The product being then heated in a water-bath, the stream of chlorine was continued for two hours. After standing in a stoppered bottle for twelve hours, it still smelt strongly of chlorine. The excess of chlorine and the hydrochloric acid formed were finally expelled by a stream of dry carbonic acid at 100° C., and the product was purified as before.

	Grm.		Grm.		Grm.	
I.	0·4853	gave	0·4334	carbonic acid and	0·1572	water.
II.	0·3299	„	0·3228	„ „	0·1137	„
III.	0·4241	„	0·3850	„ „	0·1368	„
IV.	0·5011	„	1·2995	chloride of silver.		
V.	0·3940	„	0·2274	sulphate of baryta.		
VI.	0·6996	„	0·4031	„ „		
VII.	0·4942	„	0·2810	„ „		

Found.

	I.	II.	III.	IV.	V.	VI.	VII.	*mean.*
C	23·76	23·66	24·76	„	„	„	„	24·06
H	3·59	3·83	3·59	„	„	„	„	3·67
Cl	„	„	„	64·15	„	„	„	64·15
S	„	„	„	„	7·91	7·89	7·79	7·86
								99·74

The possible substance, whose composition approaches most nearly to this, is the *chlorosulphide of terchloramylene*,

$$C_{10}\begin{Bmatrix}H_7\\Cl_3\end{Bmatrix}SCl,$$

or, according to what has been shown concerning the ethylene compounds, the *sulphide of quadrochloramyl*,

$$C_{10}\begin{Bmatrix}H_7\\Cl_4\end{Bmatrix}S;$$

for these two bodies, to whose identity analogy points, require

C_{10}	..	26·66
H_7	..	3·11
Cl_4	..	63·11
S	..	7·11
		99·99

The sulphide of quadrochloramyl or chlorosulphide of terchloramylene closely resembles in smell, taste, and physical properties the ethylene substitution-products already discussed. It is a transparent, non-volatile, light yellow liquid of specific gravity 1·406 at 16° C. It is insoluble in water, miscible with ether, and soluble in hot alcohol.

Fourteen grammes of amylene were gradually mixed at the closed end of a combustion-tube, four feet long, with more than three equivalents of bisulphide of chlorine. The mixture, having been kept boiling for eight hours (during which hydrochloric acid was copiously evolved) was transferred to a retort and heated till its temperature rose to 190° C. After cooling and decanting from the small quantity of separated sulphur, the product was washed with aqueous caustic soda, etc.

0·4118 grm. gave 0·4411 grm. of carbonic acid and 0·1680 grm. water.

0·7006 grm. gave 0·6362 grm. of chloride of silver.

These numbers show 28·76 per cent. of carbon, 4·50 per cent. of hydrogen, and 22·46 per cent. of chlorine; a result which points to no simple formula. The product was probably a mixture.

It is very worthy of notice that the body resulting from the action of chlorine upon the bisulphochloride of amylene is not an

analogue of that derived by chlorine from the bisulphochloride of chlorethylene (*i.e.* from the bisulphide of bichlorethyl) and from the bisulphide of ethyl. Comparing their general formulæ, we have for the first $C_{2n}\left\{\begin{matrix}H_{2n-4}\\Cl_4\end{matrix}\right\}S$, and for the second $C_{2m}\left\{\begin{matrix}H_{2m-3}\\Cl_3\end{matrix}\right\}S$.

But this difference, which might seem to indicate an anomalous behaviour in the two cases, really results from the symmetry of the two recompositions effected by chlorine; a symmetry which extends moreover, to the chlorine-substitution-products of the monosulphide of ethyl, studied by Regnault.* Putting the reations together:—

By the action of Chlorine.

	(1.)	(2.)	(3.)	(4.)
	C_4H_5S	$C_4H_5S_2$	$C_4\left\{\begin{matrix}H_3\\Cl\end{matrix}\right\}S_2Cl$	$C_{10}H_{10}S_2Cl$
is converted into	$C_4\left\{\begin{matrix}H\\Cl_4\end{matrix}\right\}S$	$C_4\left\{\begin{matrix}H_2\\Cl_3\end{matrix}\right\}S$	$C_4\left\{\begin{matrix}H_2\\Cl_3\end{matrix}\right\}S$	$C_{10}\left\{\begin{matrix}H_7\\Cl_4\end{matrix}\right\}S$
by the exchange of	4 H for 4 Cl	3 H for 3 Cl and SCl for Cl	H for Cl and SCl for Cl	3 H for 3 Cl Cl for SCl

Thus in all cases but the third, a fourfold exchange is effected; and that here, merely a twofold exchange occurs, may be attributed to the body, reckoned from the bisulphide of ethyl, having already suffered a two-fold replacement. It has been already shown in the first paper, that SCl is monomolecular, and may be replaced by a single atom of chlorine. Particularly remarkable is the analogy between (2) and (4), proving as it does, that these two substances are, *towards chlorine*, isotypic.

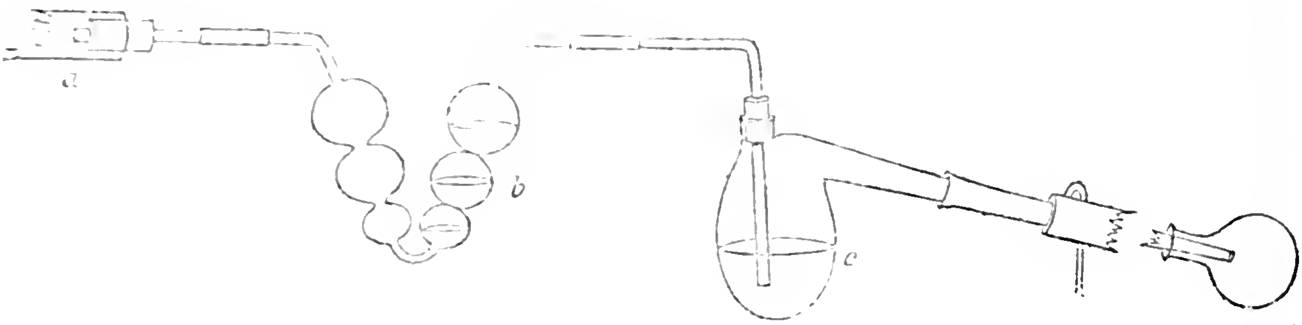
The above bodies, furnish examples of the proneness which chlorine has to replace even numbers of molecules.

In order to throw some more light upon the constitution of bisulphochloride of amylene, I have subjected that body to the action of nitric acid; but before describing the products obtained by this reaction, it will be well to consider briefly, the action of nitric acid upon amylene itself.

The temperature at which nitric acid and amylene act upon one another, is so far above the boiling point of the latter body, that great loss of amylene results if the two are heated together,

* Ann. Ch. Phys. [3], lxxi, 387.

even in capacious vessels, until the reaction commences. If five or six grammes of amylene be shaken in a bolt-head, with four or five times the volume of fuming nitric acid, and heat be applied until the acid boils, a sudden evolution of nitrogen-oxides results, the neck of the bolt-head becomes coated with a thin layer of fatty white crystals, and green oily drops, heavier than nitric acid, appear in that liquid. For the above-mentioned reason, however, this method of tracing the reaction was abandoned, and the following one employed.



Air, dried by passing over chloride of calcium, in the tube *a*, is made to bubble through amylene, contained in the bulbs *b*, and being thus charged with the vapour of amylene, it is led through fuming nitric acid in the retort *c*, which has previously been heated to boiling, and which is kept so during the passage of the gas. The retort is connected with a condenser. If the volume of the nitric acid be about seven times as great as that of the amylene, and if the current of air and the heat of the retort be so regulated, that the amylene and nitric acid are volatilized nearly together, almost the whole of the non-gaseous products consists of the white fatty crystalline substance before mentioned, which coats the surface of the receiver; the greater quantity, however, is deposited in the tube of the condenser, and may thence be washed into the receiver. Water is added to the latter, and it is vigorously shaken until the product cakes together.

Although heavier than water, it generally floats upon its surface, owing to the presence of small gas-bubbles. After washing with cold water on a funnel, and drying between blotting paper, it is strongly pressed to remove traces of the liquid product mentioned before, and then recrystallized from boiling anhydrous ether. If the ethereal solution be allowed to cool without evaporation, the substance crystallizes out in long rectangular prisms. If the

crystallization be helped by evaporation, it separates as flat rectangular tables. Under the microscope, no other than right angles could be observed in either case.

Burnt with oxide of copper, metallic copper being employed in the anterior of the tube,

I. 0·3680 grm. gave 0·5019 grm. carbonic acid, and 0·2066 grm. water.

II. 0·1330 grm. gave 19·1 cc. of nitrogen at 0° C., and 760 mm.

	Calculated.	I.	II.
C_{10} . .	37·09	37·20	„
H_{10} . .	6·18	6·24	„
N_2 . .	17·28	„	18·04
O_8 . .			

This substance may, therefore, be called binitroxamylene, its formula being—

$$C_{10}H_8 2(NO_4)$$

A portion of the nitric acid is deoxidized to NO_2; this combines with the oxygen of the excess of air to form NO_4; and the latter molecule unites directly with a fresh portion of amylene. This same substance, which can be obtained only in small quantities by the above process, may be prepared in any desired quantity by the direct union NO_4 with amylene. The latter method of preparing this body, together with some of its properties, will appear in the next communication.

VII.—*On the Crystallised Hydrates of Baryta and Strontia*

By Charles L. Bloxam.

Considerable difference of opinion appears to exist among chemical authors with respect to the composition of the crystallised hydrates of baryta and strontia, some representing them as containing 8 eqs., others 9 eqs., and others even 10 eqs. of water, whilst in some cases these hydrates, so closely analogous in their chemical relations, are represented as crystallising with different amounts of water.

Having had occasion to satisfy myself with respect to their true composition, I beg to submit the results of my analysis to the Society.

The crystallised hydrate of baryta was prepared according to the method recommended by Mohr, by adding powdered nitrate of baryta to a boiling solution of an equivalent quantity of hydrate of soda. The crystals which separated from the cooled liquid were purified by two crystallisations.

On examining the solution from which the first crop of crystals had been deposited, it was found to contain a considerable quantity of undecomposed nitrate of baryta, together with some hydrate of soda, showing that the decomposition of the nitrate by a single equivalent of soda was far from complete. In a second preparation 1·4 eqs. of hydrate of soda were employed, but in this case also, a considerable quantity of the nitrate of baryta was left undecomposed, though less than in the first experiment.

The hydrate of baryta exhibited, in a remarkable degree, the tendency to remain, without crystallising, in a super-saturated solution, until it was either briskly stirred or placed in contact with a crystal of the hydrate.

On attempting to dry the crystals in vacuo over oil of vitriol, they soon became opaque, which was at first attributed to the formation of a thin film of carbonate, but was afterwards found to arise from loss of water; indeed the crystals were found to effloresce even in air of ordinary humidity, which may help to explain the discrepancy in the results which they have afforded to different analysts.

In order to determine the amount of water lost in vacuo over oil of vitriol, separate samples of the crystals, obtained in two distinct operations, were exposed in a receiver of air over quick lime, and weighed at short intervals, until the loss of weight in a given period suddenly diminished, and the first sign of efflorescence began to show itself upon the edges of the crystals.

Two determinations of adhering water made in this way gave respectively 1·39 and 1·24 per cent.

The dry crystals were then exposed in vacuo, over oil of vitriol, until they ceased to lose weight.

The effloresced hydrate thus obtained was heated to dull redness in a closely covered silver crucible, and weighed, at intervals of four or five minutes, until it began to increase in weight slightly, from absorption of carbonic acid.

The baryta was also precipitated and determined as sulphate, both in the original dry crystals and in the effloresced hydrate.

The subjoined table contains the results of these experiments, calculated for 100 parts of the dry crystallised hydrate.

	I	II	III	IV	V	VI	Mean.		Calculated (Ba = 68·5) BaO,HO + HO + 7Aq.	
Water lost in vacuo	39·36	39·30	39·69	39·84	39·63		39·56	45·59	40·00	45·71
,, ,, on ignition	5·93	6·04	6·12				6·03		5·71	
Baryta				48·12	48·12	48·26	48·26			48·57

These numbers appear to warrant the conclusion that the formula of the crystallised hydrate of baryta is BaO,HO + 8Aq., and that of the effloresced hydrate BaO,HO + Aq, the pure hydrate BaO,HO being obtained by igniting the latter.

The effloresced hydrate suffered no more loss of water at 212° F, even in vacuo.

It is worthy of notice that this effloresced hydrate evolved much heat when moistened with water.

The crystallised hydrate of strontia was also prepared by decomposing the nitrate of strontia with hydrate of soda at the boiling point; in this case nearly 2 eqs. of the hydrate were employed for each equivalent of nitrate of strontia, and this salt was found to have been completely decomposed. The hydrate of strontia, however, did not dissolve in the liquid, like the hydrate of baryta, but separated in the form of a granular precipitate, which had the same composition as the crystallised hydrate. On pouring off the solution containing the nitrate of soda, and boiling this granular precipitate with successive portions of water, very large and beau-

tiful crystals were obtained, which were purified by recrystallisation.

The crystals effloresced in the same way as those of hydrate of baryta. They were analysed in a similar manner, the strontia being completely precipitated by sulphuric acid and alcohol, and the sulphate of strontia subsequently washed with alcohol.

The results are seen in the following table.

	I	II	III	IV	Mean.		Calculated (Sr = 43·8) SrO,HO + HO + 7Aq.	
Water lost in vacuo	47·79	47·75			47·77	60·40	47·44	61·00
" " on ignition	12·61	12·65			12·63		13·56	
Strontia	39·12	39·04	39·12	39·06			39·00	

It appears then, as would be expected, that the formula of the crystallised hydrate of strontia is SrO,HO + 8Aq, and that of the effloresced hydrate SrO,HO + Aq, but that when this latter is heated to dull redness, it loses the whole of its water, anhydrous strontia being left.*

The effloresced hydrate did not lose any more water in the water-oven at 212° F, but when raised to this temperature in vacuo, it lost 12·89 per cent., or exactly one equivalent of water, thus becoming converted into the simple hydrate SrO,HO.†

Both this and the effloresced hydrate evolved heat when moistened with water.

The inferior power possessed by strontia to retain these two last equivalents of water, is another interesting example of the gradation constantly observed in the properties of baryta and strontia; and I must express my regret that want of leisure precludes me, for the present, from examining the crystallised hydrate of lime, which may be expected to occupy a still lower position with respect to its power of retaining water of crystallisation.

* I find that this circumstance had been already pointed out by **Denham Smith** (Phil. Mag. [3], ix, 87), although chemical writers have still represented the hydrate of strontia as permanent at a red heat.

† The effloresced hydrate also lost nearly the whole of its second equivalent of water when exposed for a very long time over very concentrated oil of vitriol, in vacuo.

VIII.—*Miscellaneous Observations.*

By A. W. Hofmann.

II.

(Continued from Vol. X., p. 211.)

4. *Action of Nitrous Acid upon Nitrophenylene-diamine.*

The experiments of Gottlieb have shown that dinitrophenylamine, when boiled with sulphide of ammonium, is converted into a remarkable base crystallising in crimson needles, generally known as *Nitrazophenylamine,* and for which, in accordance with the views I entertain regarding its constitution, I now propose the name *Nitrophenylene-diamine.* I owe to the kindness of Dr. Vincent Hall a considerable quantity of this substance which is not quite easily procured. In preparing it, Dr. Hall has, in the first place, followed the succession of processes recommended by Gottlieb, viz., treatment of phenyl-citraconimide (citraconanile) with nitro-sulphuric acid, transformation of the nitro-substitute into dinitrophenylamine, and the reduction of the latter by sulphide of ammonium. In other experiments Dr. Hall has availed himself with the same advantage of phenyl-succinimide (succinanile), which, under the influence of a mixture of nitric and sulphuric acid, exhibits a deportment similar to that of the citraconyl-body. Dinitrophenyl-succinimide is readily transformed into dinitrophenylamine, which ultimately yields the crimson-coloured compound.

To the accurate description which Gottlieb has given of the preparation and the properties of this substance, I have scarcely to add a single word. The following remarks refer to an experiment made with the view of obtaining some insight into the molecular construction of the body. If, bearing in mind the numerous analogies of the radicals ethyl and phenyl, we assume that the latter by the loss of hydrogen may be converted into a diatomic molecule phenylene, C_6H_4,* corresponding to ethylene, the existence of a group of phenylene-bases corresponding to the ethylene-bases cannot be doubted.

* $H=1$, $C=12$, $O=16$, $S=32$, etc.

Ethylamine $\left.\begin{matrix} C_2H_5 \\ H \\ H \end{matrix}\right\} N$ Ethylene-diamine $\left.\begin{matrix} (C_2H_4)'' \\ H_2 \\ H_2 \end{matrix}\right\} N_2$

Phenylamine $\left.\begin{matrix} C_6H_5 \\ H \\ H \end{matrix}\right\} N$ Phenylene-diamine $\left.\begin{matrix} (C_6H_4)'' \\ H_2 \\ H_2 \end{matrix}\right\} N_2.$

The compound known as semibenzidam or azophenylamine, which Zinin obtained by exhausting the action of sulphide of ammonium on dinitrobenzol, agrees with the last-named body in composition. Those chemists, however, who have had an opportunity of becoming acquainted with the well-defined properties of ethylene-diamine, will not easily be persuaded to consider the uncouth dinitrobenzol-product, sometimes appearing in brown flakes, sometimes as a yellow resin rapidly turning green in contact with the air, as standing to phenylamine in a relation similar to that which obtains between ethylene-diamine and ethylamine. We much more readily admit a connection of this description between phenylamine and Gottlieb's crimson-coloured base, in which the clearly pronounced character of the former is still distinctly visible, although of necessity, modified by the further substitution which has taken place within the radical.

Phenylamine $\left.\begin{matrix} C_6H_5 \\ H \\ H \end{matrix}\right\} N$

Phenylene-diamine (?) $\left.\begin{matrix} (C_6H_4)'' \\ H_2 \\ H_2 \end{matrix}\right\} N_2$

Nitrophenylene-diamine $\left.\begin{matrix} (C_6[H_3, NO_2])'' \\ H_2 \\ H_2 \end{matrix}\right\} N_2.$

Does the latter formula really represent the molecular constitution of the crimson needles? The degree of substitution of this body might have been determined by the frequently adopted process of ethylation. But even a simpler and shorter method appeared to present itself in the beautiful mode of substituting nitrogen into the place of hydrogen, lately discovered by P. Griess. The red crystals undergo indeed with the greatest facility the transformation, which he has proved already for a great many derivatives of ammonia.

On passing a current of nitrous acid into a moderately concentrated solution of the nitrate of the base, the liquid becomes gently heated, and deposits, on cooling, a considerable quantity of brilliant white needles, the purification of which presents no difficulty; being sparingly soluble in cold, readily soluble in boiling water, the new compound requires only to be once or twice re-crystallised. Thus purified, the new substance forms long prismatic crystals frequently interlaced, white as long as they are in the solution, but assuming a slightly yellowish tint when dried, and especially when exposed to 100°; they are readily soluble both in alcohol and in ether. The new body exhibits a distinctly acid reaction; it dissolves on application of a gentle heat in potassa and ammonia, without, however neutralizing the alkaline character of these bases; it also dissolves in the alkaline carbonates, but without expelling their carbonic acid. The new acid fuses at 211° C., and sublimes at a somewhat higher temperature, with partial decomposition. The sublimate consists of small prismatic crystals. Analysis gave the following results:—

I. 0·3290 grm. acid dried at 100°, gave
0·5298 „ carbonic acid, and
0·0777 „ water.

II. 0·2868 grm. acid gave 84 cc. moist nitrogen at 15°, and 0·7583 Bar. (corr.)

These numbers lead to the ratio:—

$$C_3H_2N_2O,$$

and, the origin of the substance being taken into consideration, to the formula:—

$$C_6H_4N_4O_2.$$

	Theory.		Experiment. I.	Experiment. II.
C_6	72	43·90	43·92	—
H_4	4	2·44	2·62	—
N_4	56	34·15	—	34·32
O_2	32	19·51	—	—
	164	100·00		

This formula is confirmed by the analysis of the silver- and of the potassium-compound.

Silver-salt. This salt is obtained in the form of a white amorphous precipitate on mixing the saturated ammonia-solution of the acid with nitrate of silver. *In vacuo* this salt may be dried without decomposition; at 100° it becomes slightly coloured; when gently heated on platinum foil it detonates. The silver therefore had to be estimated as chloride.

I.	0·4215	grm.	silver-salt gave
	0·4068	,,	carbonic acid, and
	0·0487	,,	water.
II.	0·2984	,,	silver-salt gave
	0·1574	,,	chloride of silver.

The formula $C_6[H_3Ag]\,N_4O_2$ involves the following values :—

		Theory.	Experiment. I.	Experiment. II.
C_6	72	26·57	26·32	—
H_3	3	1·11	1·28	—
Ag	108	39·85	—	39·67
N_4	56	20·66	—	—
O_2	32	11·81	—	—
	271	100·00		

Potassium-salt. Obtained in pretty well-formed, flattened prisms, by saturating a moderately concentrated boiling solution of potassa with the acid; the crystals are difficultly soluble in potassa, but exceedingly soluble in pure water and in alcohol; the recrystallization is therefore attended with very considerable loss. The aqueous solution of the salt yields a crystalline precipitate on addition of potassa. The salt, even after four or five recrystallizations from alcohol, retains a distinctly alkaline reaction. Its composition was fixed by a potassium determination.

0·2012	grm.	salt dried at 100° gave
0·0857	,,	sulphate of potassium.

The formula $C_6 [H_3K] N_4O_2$ requires the following values :—

	Theory.		Experiment.
C_6	72	35·64	—
H_3	3	1·48	—
K	39	19·31	19·10
N_4	56	27·72	—
O_2	32	15·85	—
	202	100·00	

With regard to the other salts, I have made but few observations.

The ammonium-salt crystallizes in needles. It has, however, but little stability, losing the whole of the ammonia when repeatedly recrystallized. The solution of this salt exhibits with metallic oxides the following deportment.

Barium and calcium-salts are not precipitated. Salts of copper give a light blue, salts of nickel a light green precipitate. The solution of a ferrous salt produces a deep brown-red precipitate, probably with simultaneous decomposition of the acid; the solution of a ferric salt, a light fawn-coloured precipitate. The salts of lead, zinc, manganese, and mercury (*mercurosum* and *mercuricum*), furnish white flaky precipitates.

The analysis of the new compound shows that, under the influence of nitrous acid on nitrophenylene-diamine, one molecule of nitrogen is substituted into the place of three molecules of hydrogen, which are eliminated in the form of water

$$\underbrace{C_6H_7N_3O_2}_{\text{Nitrophenylene-diamine.}} + HNO_2 = 2\,H_2O + \underbrace{C_6[H_4N]N_3O_2}_{\text{New acid.}}$$

I do not propose a name for the new compound, which can claim but a passing interest, as throwing by its formation some light on the constitution of nitrophenylene-diamine.

The composition of the new acid and of its salts shows that in the crimson base four hydrogen molecules are still capable of replacement; in other words, that this body still contains four extra-radical molecules of hydrogen. These experiments appear to confirm the view which in the commencement of this note,

I have taken of the constitution of the body; at all events, the mutual relation of the several compounds is satisfactorily illustrated by the formulæ—

$$\text{Nitrophenylene-diamine} \quad \left.\begin{matrix}(C_6[H_3NO_2])'' \\ H_2 \\ H_2\end{matrix}\right\} N_2$$

$$\text{New acid} \quad \left.\begin{matrix}(C_6[H_3NO_2])'' \\ N''' \\ H\end{matrix}\right\} N_2$$

$$\text{Silver-salt} \quad \left.\begin{matrix}(C_6[H_3NO_2])'' \\ N''' \\ Ag\end{matrix}\right\} N_2.$$

If the admissibility of this interpretation be confirmed by further experiments, the reaction discovered by Griess furnishes a new and valuable method of recognising the degree of substitution in the derivatives of ammonia.

The new acid differs in many respects from the substances similarly produced from other nitrogenous compounds. As a class, these substances are remarkable for the facility with which they are changed under the influence of acids and more especially of bases. The new acid exhibits remarkable stability; it may be boiled either with potassa or with hydrochloric acid without undergoing the slightest change. Even a current of nitrous acid passed into either the aqueous or alcoholic solution is without the slightest effect. The latter experiment was repeatedly performed; for if the action of nitrous acid in a second phase of the process had assumed the form so frequently observed by Piria and others, it might have led to the formation of the diatomic nitrophenylene-alcohol, according to the equation

$$\left.\begin{matrix}(C_6[H_3,NO_2])'' \\ H_2 \\ H_2\end{matrix}\right\} N_2 + 2HNO_2 = 2H_2O + N_4 + \left.\begin{matrix}(C_6[H_3,NO_2])'' \\ H_2\end{matrix}\right\} O_2.$$

It deserves to be noticed that nitrophenylene-diamine, although derived from two molecules of ammonia, is, nevertheless, a decidedly mono-acid base. Gottlieb's analyses of the chloride, nitrate, and sulphate, left scarcely a doubt on this point. However, as some of the natural bases, quinine, for instance, are

capable of combining either with one or with two molecules of acid, I thought it of sufficient interest to confirm Gottlieb's observations by some additional experiments. The crystals deposited on cooling from a solution of nitrophenylene-diamine in concentrated hydrochloric acid were washed with the same liquid, and dried *in vacuo* over lime.

0·3975 grm. substance gave
0·3005 ,, chloride of silver = 18·70 p. c. of chlorine.

The formula

$$\left[H \left\{ \begin{matrix} (C_6[H_3,NO_2])'' \\ H_2 \\ H_2 \end{matrix} \right\} N_2 \right] Cl$$

requires 18·73 p. c. of chlorine.

The dilute solution of the previous salt is not precipitated by dichloride of platinum; nor could the double salt of the two chlorides be obtained by evaporating the mixture of the two solutions, which, just as Gottlieb observed, was readily decomposed with separation of metallic platinum. I had, however, no difficulty in preparing a platinum-salt, crystallizing in splendid long brown-red prisms, by adding the platinum solution to the concentrated solution of the hydrochlorate.

0·4225 grm. of the platinum-salt dried *in vacuo*, left on ignition 0·115 grm. = 27·22 p. c. of platinum.

The theoretical percentage of the formula

$$\left[H \left\{ \begin{matrix} (C_6[H_3,NO_2])'' \\ H_2 \\ H_2 \end{matrix} \right\} N_2 \right] Cl,Pt\,Cl_2$$

is 27·48 p. c. of platinum.

These experiments prove that, even under the most favourable circumstances, nitrophenylene-diamine combines with only 1 eq. of acid, while the ethylene-derivatives are decidedly diacid. The diminution of saturating power in nitrophenylene-diamine at the first glance seems somewhat anomalous; but the anomaly disappears if the constitution of the body be more accurately examined. It cannot be doubted that the diminution of the saturating power is due to the substitution which has taken place within the radical

of the diamine. I pointed out some time ago,* that the basic character of phenylamine itself is considerably modified by successive changes induced in the phenyl-radical by substitution. Chlorphenylamine, though less basic than the normal compound, still forms well-defined salts with the acids; the salts of dichlorphenylamine, on the other hand, are so feeble, that under the influence of boiling water they are split into their constituents; and in trichlorphenylamine the basic character has entirely disappeared. Again, on examining the nitro-substitutes of phenylamine, we find that even nitrophenylamine is an exceedingly weak base, whilst dinitrophenylamine is perfectly indifferent. What wonder, then, that a molecular system, to which, in the normal condition, we attribute a diacid character, should, by the insertion of special radicals, be reduced to monoacidity? The normal phenylene-diamine, which remains to be discovered, will, doubtless, be found to be diacid, like the diamines derived from ethylene. Even now the group of diacid diamines is represented in the naphtyl-series.

$$\text{Naphtylamine} \qquad \left.\begin{matrix} C_{10}H_7 \\ H \\ H \end{matrix}\right\} N, \text{ monoacid.}$$

$$\text{Naphtylene-diamine} \qquad \left.\begin{matrix} (C_{10}H_6) \\ H_2 \\ H_2 \end{matrix}\right\} N_2, \text{ diacid.}$$

The body which I designate by the term naphtylene-diamine is the base which Zinin obtained by the final action of sulphide of ammonium upon dinitronaphtalin. This substance, originally designated as seminaphtalidam, and subsequently described as naphtalidine, combines, according to Zinin's experiments, with two equivalents of hydrochloric acid.†

I must add a remark suggested by the perusal of an interesting paper lately published by Kolbe.‡ In this paper, Kolbe refers to an outline of the history of ammonia and its derivatives, which, in the form of an evening lecture, I gave to the members of this Society, and which was subsequently printed in this journal.§ Kolbe regards many of the ammonia-compounds from a different point of view and expresses them by molecular

* Mem. of Chem. Soc., ii, 298.

† Ann. Ch. Pharm. lxxxv, 328.

‡ Ueber den natürlichen Zusammenhang der organischen mit den unorganischen Verbindungen.—Ann. Ch. Pharm. cxiii, 293.

§ Chem. Soc. Qu. J. xi, 252.

formulæ different from those which I have adopted. It is not my intention to refer in detail to the several questions which he discusses, more especially since many of the theoretical views in which we differ were brought forward by others, and were simply introduced into the sketch with the view of rendering it as complete as possible; yet I must not allow this opportunity to pass without a word or two in elucidation of a question on which we differ more in appearance than in reality.

In classifying the basic ammonia-derivatives, I proposed to designate the substances formed by the coalescence of more than one molecule of ammonia, in accordance with the nomenclature adopted for the neutral derivatives, and to distinguish, as monamines, diamines, and triamines, the bases derived from one, two, or three molecules of ammonia. In a classification of this kind the circumstance could not be left unnoticed, that many of the diamines and triamines combine with one equivalent of acid only, instead of saturating, as might have been expected from their construction, two or three equivalents. I was thus naturally led to subdivide again, and to distinguish, for instance, monoacid and diacid diamines, and I added: "It is obvious that the question, whether a diamine is capable of uniting with one or two equivalents of acid, must be intimately connected with the molecular construction of the basic system. As yet the nature of this connection remains unknown."

In the paper quoted, Kolbe remarks: "There appears no reason why, among the bodies derived from two molecules of ammonia, there should be, side by side with the diatomic substances, others yielding monoatomic ammonium-compounds. I cannot, therefore, consent to regard the ureas, melaniline, and other bases containing two atoms of nitrogen, as true diamines."

It is scarcely necessary to state that I entirely agree with my friend if he views as true diamines those bases which unite with two equivalents of acid; for it is proved experimentally, that the ureas and melaniline combine with one equivalent of acid only. All depends upon the definition of the word diamine. I had designated by this name basic compounds derived from two molecules of ammonia, without reference to the degree of saturating power; and even now it appears to me somewhat arbitrary to limit this term to those substances which unite with two equivalents of acid, especially since there are diatomic bases which are capable of combining either with one or with two equivalents of acid.

5. *Action of Bisulphide of Carbon upon Amylamine.*

In a note on the alleged transformation of thialdine into leucine, communicated some time ago* to the Chemical Society, I alluded to a crystalline substance observed by Wagner, when he submitted amylamine to the action of bisulphide of carbon. Wagner had not analysed this substance, but, considering its mode of formation, he had suggested that it might possibly be thialdine:

$$\underset{\text{Amylamine.}}{C_5H_{13}N} + CS_2 = \underset{\text{Thialdine.}}{C_6H_{13}NS_2}\dagger$$

A simple comparison of the properties of thialdine with those of the substance produced by the action of bisulphide of carbon upon amylamine, had enabled me at once to recognise the difference between the two bodies; and, satisfied with the result, I had not at the time examined more minutely into the nature of the latter substance.

The new interest conferred by recent researches upon leucine and its homologues, has recalled my attention to the sulphuretted derivative of amylamine.

This body may be readily procured by mixing anhydrous amylamine with a solution of dry bisulphide of carbon in anhydrous ether. The mixture becomes warm, and deposits, on cooling, white shining scales, which are insoluble in ether, and may therefore be purified by washing them with this liquid. The new body is likewise insoluble in water, but readily dissolves in alcohol; when dry, it may be exposed for a while to a temperature of 100° C. without fusing; after some time, however, the substance begins to be liquefied and to undergo complete decomposition, sulphuretted hydrogen being evolved. The same change occurs, although more slowly, at the common temperature; a mixture of free sulphur with a new crystalline body, extremely fusible, insoluble in water, but soluble both in alcohol and ether, remaining behind.

I. 0·274 grm. of the amylamine-body burnt with a mixture of oxide of copper and chromate of lead, gave 0·535 grm. of carbonic acid, and 0·2535 grm. of water.

* Chem. Soc. Qu. J. x, 193.

† $H = 1$, $C = 12$, $O = 16$, $S = 32$.

II. 0·429 grm. of substance, dissolved in alcohol and boiled for some time with nitrate of silver, gave 0·837 grm. of sulphide of silver.

These numbers lead to the formula

$$C_{11}H_{26}N_2S_2 = C_6H_{13}NS_2,C_5H_{13}N.$$

	Theory.		Experiment. I.	Experiment. II.
C_{11}	132	52·8	53·25	—
H_{26}	26	10·4	10·28	—
N_2	28	11·2	—	—
S_2	64	25·6	—	25·17
	250	100·0		

The new substance then is formed simply by the union of two molecules of amylamine with one molecule of bisulphide of carbon.

$$\underbrace{2C_5H_{13}N}_{\text{Amylamine.}} + CS_2 = \underbrace{C_{11}H_{26}N_2S_2}_{\text{New compound.}}$$

A glance at this formula suffices to characterize this substance as amyl-sulphocarbamate of amylammonium.

$$C_{11}H_{26}N_2S_2 = \left.\begin{matrix}[(CS)''\ (C_5H_{11})\ HN]\\ [(C_5H_{11})\ H_3N]\end{matrix}\right\} S.$$

This view is readily confirmed by experiment. Addition of hydrochloric acid to the crystalline compound immediately separates an oily liquid which gradually solidifies, and the acid solution then contains amylamine which may be liberated by potassa. The oily substance is obviously amyl-sulphocarbamic acid. This body is readily soluble in ether, by which it may be separated from the chloride of amylammonium; it dissolves in ammonia and in potassa; mixed with amylamine it reproduces the original crystalline compound.

Experiments with ethylamine have furnished perfectly analogous results. I have been satisfied to establish qualitatively the analogy of the reactions.

It is of some interest to compare the deportment of amylamine under the influence of bisulphide of carbon with that of phenylamine in the same conditions. If these two bodies gave rise to

similar changes, we should expect, in the case of phenylamine, the formation of phenyl-sulphocarbamate of phenylammonium. But experiment proves that phenylamine produces diphenyl-sulphocarbonyl-diamide (sulphocarbanilide), sulphuretted hydrogen being evolved :—

$$\underbrace{2C_6H_7N}_{\text{Phenylamine.}} + CS_2 = \underbrace{C_{13}H_{12}N_2S}_{\text{Diphenyl-sulpho-carbonyl-diamide.}} + H_2S.$$

Nevertheless it is extremely probable that further experiments will establish the perfect analogy in the deportment of amylamine and phenylamine with bisulphide of carbon. Diphenyl-sulphocarbonyl-diamide is probably the product of decomposition of a very unstable phenyl-sulphocarbamate of phenylammonium—

$$\underbrace{C_{13}H_{14}N_2S_2}_{\text{Phenyl-sulphocarbamate of phenylammonium.}} = H_2S + \underbrace{C_{13}H_{12}N_2S,}_{\text{Diphenyl-sulphocarbonyl-diamide.}}$$

while a more minute examination of the crystalline substance obtained by the action of heat upon amyl-sulphocarbamate of amylammonium cannot fail to characterize it as diamyl-sulphocarbonyl-diamide.

$$\underbrace{C_{11}H_{26}N_2S_2}_{\text{Amyl-sulphocarbamate of amylammonium.}} = H_2S + \underbrace{C_{11}H_{24}N_2S}_{\text{Diamyl-sulphocarbonyl-diamide.}}$$

The apparent dissimilarity of the two reactions would thus be reduced to the unequal stability of the sulphocarbamic acids of the amyl- and phenyl-series.

6. *On the use of Pentachloride of Antimony in the Preparation of Chlorine-compounds.*

Under a cloudless sky nobody would think of preparing the tetrachloride of carbon by any other process than by acting with chlorine upon chloroform. Exposed to direct sunlight, chloroform, when distilled in an atmosphere of chlorine, is rapidly converted into tetrachloride of carbon. A London November sky is, however, rather unfavourable to this process, and when requir-

ing lately, for some experiments, a small quantity of the tetrachloride, I was compelled to have recourse to another method. A well-known process, for which we are indebted to Prof. Kolbe, consists in submitting the bisulphide of carbon to the action of chlorine at a red heat, when chloride of sulphur and chloride of carbon are formed. I have repeatedly availed myself of this process, which, when a large quantity of chloride of carbon is to be prepared, leaves nothing to be desired. When, however, a small amount is rapidly required, the apparatus involved in this process becomes rather inconveniently troublesome.

I have, therefore, endeavoured to substitute chlorine in a state of combination for the free chlorine. Pentachloride of phosphorus, as is well known, exerts so little action upon bisulphide of carbon, that it has been found convenient to prepare the pentachloride of phosphorus by saturating a solution of phosphorus in bisulphide of carbon with chlorine gas. There is likewise, no reaction between pentachloride of phosphorus and bisulphide of carbon at 100° under pressure; it is only at a higher temperature that an action takes place. A very different result is obtained when the latter compound is submitted to the action of pentachloride of antimony, the chlorinating properties of which were first noticed by Wöhler.

On adding pentachloride of antimony to bisulphide of carbon, a transparent mixture is obtained, which exhibits, after a few minutes, a powerful reaction, becoming very hot, and assuming a dark reddish-brown colour; the mixture deposits on cooling a copious crystallization of terchloride of antimony, interspersed with well-formed sulphur-crystals. The liquid poured off from the crystals consists chiefly of tetrachloride of carbon, retaining some bisulphide of carbon, chloride of sulphur, and terchloride of antimony :—

$$CS_2 + 2SbCl_5 = CCl_4 + 2SbCl_3 + S_2.$$

I had expected that the reaction would give rise to the formation of a compound $SbCl_3S$; but I have always found that the terchloride of antimony and the sulphur are separately deposited; and the same observation was made by Mr. H. McLeod, who has frequently carried out this reaction in my laboratory, modifying the proportions and the conditions of the experiment to a considerable extent. The small quantity of chloride of sulphur, which is simultaneously formed, appears to be the product of a secondary

reaction, a portion of the pentachloride not yet acted upon being reduced by the separated sulphur.

If the experiment be made with a couple of ounces, the two liquids must be mixed in a flask provided with a vertical cooling apparatus; the reaction is so powerful, that a considerable quantity of the material would be lost without this precaution. Whilst studying this process, I have allowed the two liquids to act upon each other in various proportions: on employing 1 eq. of bisulphide of carbon (1 part by weight) and 2 eq. of pentachloride of antimony (8 parts by weight) the decomposition is pretty complete; on account of the formation of chloride of sulphur, however, the theoretical quantity of chloride of carbon is never reached. The process yields a much more copious result when the pentachloride of antimony is mixed with a considerable excess of bisulphide of carbon, and the mixture, whilst boiling in a retort, is submitted to the action of a current of chlorine gas. In this manner large quantities of bisulphide of carbon may be transformed into the tetrachloride by the intervention of a comparatively small quantity of pentachloride of antimony.

In order to purify the tetrachloride of carbon, the product of the reaction is submitted to distillation; the liquid passing over below 100° is boiled for some time with a solution of potassa, which removes terchloride of antimony and chloride of sulphur, together with any undecomposed bisulphide of carbon. From the product, boiling at a higher temperature, a considerable quantity of pure terchloride of antimony may be recovered.

The tetrachloride obtained by this process exhibits all the properties of the product obtained by other modes of preparation. It boils at 77°. The determination of the chlorine gave the following results:—

0·195 grm. of substance, ignited with lime, furnished 0·730 chloride of silver.

	Theory.		Experiment.
C	12	7·79	—
Cl_4	142	92·21	92·56.
	154	100·00	

Pentachloride of antimony may be used with advantage in many cases as a carrier of free chlorine. On heating a very moderate quantity of pentachloride of antimony in a retort connected with

an inverted cooling apparatus, and passing simultaneously currents of dry olefiant gas and chlorine through the boiling liquid, a very large amount of Dutch liquid may be obtained in an exceedingly short time. In an atmosphere of pentachloride of antimony, the combination of the ethylene and the chlorine goes on with the greatest facility. As soon as the retort is filled with the Dutch liquid, the access of the two gases is interrupted, and the liquid distilled. The portion boiling below 100° requires only to be once more rectified in order to furnish perfectly pure bichloride of ethylene. The residue in the retort consists of a mixture of terchloride and pentachloride of antimony, which may serve for a new experiment.

The preparation of large quantities of pentachloride of antimony presents no difficulty whatever, since antimony combines readily with chlorine at the common temperature. A simple mode of proceeding consists in introducing the antimony, coarsely powdered, into a combustion-tube from 5 to 6 feet long, rising at an angle of 10° or 15°, one end of which is fitted into one tubulature of a two-necked glass globe, the other neck of the globe communicating with a tube supplying dry chlorine gas. The combination taking place in the tube, the product flows backwards into the globe, whilst the long layer of antimony prevents the escape of any chlorine.

7. *On Di-iodide of Methylene.*

Being engaged in some experiments on the action of chloride of carbon CCl_4 on the phosphorus-bases, I thought it desirable to study likewise the deportment of these substances under the influence of the corresponding iodide. Bearing in mind the facility with which chloroform is converted into chloride of carbon, I had some hope of procuring the iodide by the action of dry iodine upon iodoform:—

$$CHI_3 + I_2 = HI + CI_4 \ (?)$$

When a mixture of iodoform and iodine, in the equivalent proportions of the above equation, was exposed in sealed tubes to a temperature of from 140° to 150° C., the iodoform was found to be changed after the lapse of some hours. On opening the tubes, an acid gas was evolved; and on distilling the dark solid residue with

water, an aromatic body passed over, which collected in the receiver in the form of heavy oily drops. Decolorized by potassa and freed from water by chloride of calcium, the oily body boiled at about 180°, a considerable portion being decomposed, with evolution of hydriodic acid, and the distillate reassuming the red coloration. The liquid was therefore distilled *in vacuo;* it then passed over colourless, and without decomposition, at a temperature scarcely higher than the boiling point of water.

I. 1·222 grm. of substance, burnt with chromate of lead, gave 0·2077 grm. of carbonic acid, and 0·0800 grm. of water.

II. 0·705 grm. of substance burnt with lime, furnished 1·243 grm. of iodide of silver.

These numbers represent the composition of di-iodide of methylene—

$$CH_2I_2$$

only recently discovered by Boutlerow.*

	Theory.		Experiment. I.	Experiment. II.
C	12	4·48	4·63	—
H_2	2	0·74	0·73	—
I_2	254	94·78	—	95·27
	268	100·00		

The compound analysed was indeed pure di-iodide of methylene. At a temperature near the freezing point of water, it solidified in large crystalline plates, and exhibited in every respect the properties described by Boutlerow. The analysis of the substance received moreover additional confirmation in a variety of substitutions in which it was subsequently employed.

The idea naturally suggested itself that the free iodine had no share in the formation of the di-iodide of methylene in the process described, but that the transformation of the iodoform was exclusively due to the action of heat. Experiment has verified this anticipation. Iodoform, when heated by itself in sealed tubes, at a temperature of 150°C. for several hours, furnished, on subsequent distillation with water, a very appreciable quantity of di-iodide of methylene. A comparative experiment, in which I followed the plan recommended by Boutlerow (1 eq. of iodoform, and 3 eqs. of ethylate of sodium), leads me to think that the action of heat

* Compt. rend. xlvi, 595.

yields a larger product and involves on the whole a far less troublesome operation. The inequality of the amount of product in my experiments, however, may possibly be ascribed to the circumstance that I have repeatedly prepared the methylene-compound by exposing iodoform to the action of heat alone, while Boutlerow's process was only once or twice adopted.

The transformation of iodoform into di-iodide of methlene by one or other of these processes is strange enough, and as yet remains entirely unexplained; there is formed, together with the methylene-compound, a quantity of a brown substance, the nature of which appears anything but attractive.

8. *Dibromide of Ethylene.*

The usual mode of preparing this compound, which of late has acquired considerable interest, consists in passing ethylene into bromine covered with a layer of water. This method is extremely tedious, since, in order to avoid the loss of both bromine and of ethylene, the gas can be but slowly transmitted through the liquid. The compound may, however, be rapidly obtained without the slightest loss, by an exceedingly simple modification of the process.

A strong glass bottle, of 2 or 3 litres capacity, is provided with a perforated cork, through which is fitted a glass tube open at both ends, one of which reaches nearly to the bottom of the bottle, whilst the other, slightly projecting over the cork, communicates by means of a flexible india rubber tube with the gasholder containing the ethylene. To start the operation, the bottle is detached, and filled over water with ethylene gas, into which are then poured from 100 to 130 grm. of commercial bromine, and about half that quantity of water, the cork with the glass tube being immediately replaced. On gently agitating the bottle, the ethylene is rapidly absorbed, and on turning the stop-cock of the gasholder, the gas rushes into the bottle exactly as into a vacuum. If the agitation be continued, a very large volume of ethylene may be thus united with bromine in an exceedingly short space of time, without the loss of a particle of the constituents or of the compound. As soon as the absorption becomes languid, the bromine is renewed, and the process continued in this manner until the accumulation of the dibromide renders it desirable to interrupt

the operation. When working upon a very large scale, it is convenient to insert between the absorption-bottle and the gasholder a wash-bottle filled with water or dilute potassa, which serves as a gauge for the rapidity of the gas-current, purifying the gas at the same time, if necessary, and intercepting, moreover, any bromine-vapour that may have risen into the india rubber tube, if the mixture should have become hot, in consequence of too rapid absorption.

9. *Metamorphosis of Monobrominated Ethylene.*

A quantity of monobrominated ethylene (bromide of vinyl) was sealed up in a glass tube with the view of preserving it. After the lapse of a night, the colourless extremely mobile liquid was found to have become a white porcelain-like mass, and on opening the tube all pressure had disappeared. The white substance was perfectly amorphous and inodorous, and proved insoluble in water, in alcohol, and in ether. When heated it was charred, with abundant evolution of hydrobromic acid.

Analysis showed, as might have been expected, that the alteration of the monobrominated ethylene had been simply molecular.

0·2954 grm. substance, burnt with chromate of lead, gave 0·24781 grm. of carbonic acid and 0·0780 grm. of water.

The values corresponding to the formula C_2H_3Br are:—

	Theory.		Experiment.
C_2	24	22·43	22·87
H_3	3	2·80	2·93
Br	80	74·77	—
	107	100·00	

The chemical relations of bromide of vinyl are as yet but slightly examined. From its formula, the body might be considered as the hydrobromic ether of an alcohol homologous to allylic alcohol; this mode of viewing it, however, is not supported by the general deportment of the compound. The peculiar molecular transformation which it undergoes points rather to aldehydic relations, aldehyde being isomeric with the alcohol in question. As in the case of aldehyde, the conditions involving these transformations are utterly unknown; I have vainly tried to fix the

circumstances under which the solid modification of bromide of vinyl is formed. In some cases the liquid bromide was preserved for weeks without the slightest change, when suddenly the liquid was found to have been transformed throughout its entire mass. At one time I thought I had observed that the presence of water favoured the metamorphosis, but I have convinced myself by special experiments that this is not the case. The change takes place as capriciously in the presence as in the absence of water.

It deserves to be noticed that other bodies derived from ethylene by substitution are prone to similar transformations. Thus Regnault,* many years ago, observed analogous phenomena in the case of dichlorinated ethylene.

10. *Iodide of Ethyl.*

The reaction generally used for the preparation of this compound is so simple and elegant, that it would be difficult to propose a better method. Indeed, all the processes which have been suggested differ only as to the proportions of iodine, phosphorus, and alcohol, or as to the manner in which these substances are to be brought into contact with each other. Iodide of ethyl being extensively used as substitution-material in all laboratories, every observation which is calculated to facilitate the preparation of this body may prove acceptable.

The common plan of gradually introducing fragments of phosphorus into the mixture of alcohol and iodine has the disadvantage of occasionally giving rise to powerful reactions, involving considerable loss of materials, even when great care is taken to add the phosphorus slowly and in little fragments. This inconvenience may be readily avoided by introducing the phosphorus, together with about a fourth of the alcohol to be used, into a retort connected with an efficient cooler, into the tubulus of which is fitted a glass globe, provided with tube and stopcock.† The rest of the alcohol is then poured upon the iodine, and the solution thus obtained is introduced through the globe into the retort, which is heated on a sand-bath or in a water-bath. Iodine is but

* Ann. Chim. Phys. lxix, 151.

† The apparatus used in the preparation of triethylphosphine may be conveniently employed.—Chem. Soc., Qu. J., xi, 60.

sparingly soluble in alcohol, but excessively so in iodide of ethyl; it is, therefore, only necessary to pour the first portion which distils upon the residuary iodine, which is readily dissolved, and to allow the concentrated iodine solution thus obtained to flow through the globe into the retort, where it is instantaneously converted into iodide of ethyl. This process is especially convenient when the iodide of ethyl is to be prepared on a rather large scale. In this case I find it convenient to dissolve the iodine at once in iodide of ethyl, and to introduce it slowly through the globe into the retort. The stopcock being appropriately adjusted, the process requires but little attention, and, being continuous, yields a very large product in a comparatively limited time. The iodide generally distils at once perfectly colourless, and requires only to be washed with water in order to become free from traces of alcohol. It deserves to be noticed that the process may be carried out in a very moderate-sized retort, since there is only a very limited portion of material at a time under operation.

Convenient proportions for iodide of ethyl are 1000 grammes of iodine, 700 grammes of alcohol, of spec. grav. 0·84 (83 per cent.), and 50 grammes of phosphorus. From 96 to 98 per cent. of the theoretical quantity of pure iodide of ethyl are obtained. It deserves to be noticed how small a quantity of phosphorus is necessary for the etherification of the iodine, the quantity stated being less than one-half of the amount given in the majority of prescriptions.

Iodide of methyl and iodide of amyl may be prepared in the same manner. In the case of iodide of methyl, the following proportions have been found by experiment to work well. 1000 grammes of iodine, 500 grammes of methylic alcohol (the fraction boiling below 74°), and 60 grammes of phosphorus. The product, owing to the volatility of the compound, is somewhat less than in the previous case, amounting to from 94 to 95 per cent. of the theoretical quantity.

11. *On the deportment of Cyanate of Ethyl with Ethylate of Sodium.*

In a former note* I have stated that cyanate of ethyl, when heated with ethylate of sodium, is converted into triethylamine and carbonate of sodium. But I have pointed out at the same time that, owing to the facility with which the ethylate of sodium

* Chem. Soc., Qu. J., x, 20.

undergoes decomposition at comparatively moderate temperatures, the process in question appeared to be of limited application.

I have lately had occasion to resume the study of cyanate of phenyl, which I described several years ago.* It appeared to me to be of some interest to apply the above reaction to the preparation of triphenylamine. On performing the experiment, I found, however, that phenylate of sodium and cyanate of phenyl give rise to a different reaction; no triphenylamine was obtained in this process.

This unexpected result induced me to repeat the experiment on the action of ethylate of sodium upon cyanate of ethyl. I have found that in this case likewise the reaction frequently assumes a form different from that which I had previously observed, and which excludes the production of triethylamine. I am engaged in the study of this transformation, the result of which I propose to lay before the Society on some future occasion.

12. *On Glycerin.*

Before the nature of this interesting compound had been finally established by Berthelot's remarkable inquiries, it had been frequently surmised, that the saponification of the several fatty bodies which are found in nature did not invariably furnish the same kind of glycerin.

This view appeared to receive new support in the researches of Wurtz, who has rendered it probable that glycerin is but the type of a class of homologous triatomic alcohols.

As a contribution towards the elucidation of this question, an experiment may be briefly mentioned which arose from a conversation with my friend Mr. George Ferguson Wilson, the technical director of the great establishment well known as Price's Patent Candle Company. Many hundred weights of glycerin are weekly separated in these works, by simple steam-saponification, from a considerable variety of fatty bodies; and Mr. Wilson, who has studied with predilection the preparation and purification of glycerin on a large scale, has acquired a sum of practical information upon this subject such as will not easily be found again. To my question, whether there is more than one kind of glycerin, Mr. Wilson replied, that in his opinion all the fatty bodies which he had examined contained the same

* Chem. Soc., Qu. J., ii, 323.

variety of glycerin, with the exception of cocoa-nut oil, the glycerin-like constituent of which differed in many respects so much from ordinary glycerin, that he was inclined to consider it as a special variety.

Since this question admitted of a simple experimental solution, Mr. Wilson kindly supplied me with a quantity of glycerin obtained by the saponification of cocoa-nut oil. This substance, although prepared in the same manner, differed in colour and odour from the glycerin furnished by other fatty substances. But notwithstanding the colouring matter, and an odorous principle which adhered with great pertinacity, it was not difficult to identify the compound under examination with ordinary glycerin. Distilled with iodide of phosphorus it furnished iodide of allyl, which exhibited the same boiling point as that obtained from ordinary glycerin, and was also transformed under the successive influence of oxalate of silver and ammonia, respectively, into oxalate of allyl and allyl-alcohol.

These experiments appear to solve the question as far as cocoa-nut oil is concerned.

13. *Dinitrotoluic Acid.*

The nitro-substitutes of the aromatic acids are but slowly transformed into dinitro-compounds. Whoever has made the experiment in the benzoyl-series has had an opportunity of experiencing this difficulty. The same remark applies to the toluyl-series: Noad,* to whom we are indebted for the first knowledge of this group, found that nitrotoluic acid may be dissolved in a boiling mixture of nitric and sulphuric acids without undergoing any alteration.

Whilst studying some reduction phenomena of nitro-compounds, I felt an interest in procuring, if possible, a small quantity of dinitrotoluic acid, and by my desire Mr. William Temple has prepared this substance. Pure nitrotoluic acid was digested for two days with three times its weight of equal parts of fuming nitric and sulphuric acids. The solution being mixed with an equal volume of water, a crystallization of dinitrotoluic acid was obtained on cooling. It was washed, recrystallized from water, and submitted to analysis.

I. 0·582 grm. of acid, burnt with oxide of copper, gave 0·908 grm. of carbonic acid and 0·152 grm. of water.

* Mem. Ch. Soc., III. 437.

II. 0·396 grm. of acid gave 0·614 grm. of carbonic acid and 0·103 grm. of water.

These numbers prove that the acid consisted of dinitrotoluic acid $C_8H_6N_2O_6 = C_8[H_6(NO_2)_2]O_2$ in a state of purity.

	Theory.		Experiment. I.	II.	Mean.
C_8	96	42·48	42·54	42·30	42·42
H_6	6	2·65	2·94	2·88	2·91
N_2	28	12·39	—	—	—
O_6	96	42·48	—	—	—
	226	100·00			

This result is fully confirmed by the analysis of the silver-salt, which is obtained in the form of a white precipitate on addition of nitrate of silver to a solution of dinitrotoluate of ammonium. The silver-salt contains

$$C_8H_5AgN_2O_6 = C_8[H_5(NO_2)_2Ag]O_2.$$

I. 0·609 grm. of silver-salt gave on combustion, 0·643 grm. of carbonic acid and 0·094 grm. of water.

II. 0·130 grm. of silver-salt gave 0·042 grm. of silver.

	Theory.		Experiment. I.	II.
C_8	96	28·83	28·78	—
H_5	5	1·50	1·71	—
Ag	108	32·43	—	32·30
N_2	28	8·41	—	—
O_6	96	28·83	—	—
	333	100·00		

14. *On Isatin.*

Few bodies have fixed the attention of chemists more generally than indigo. But have their experiments led to a satisfactory view regarding the nature of this colouring matter? The brilliant labours of Erdmann and of Laurent have brought to light a rich

harvest of the most interesting derivatives of indigo, but they have left us in uncertainty with regard to the constitution of this group of compounds.

With the hope of throwing some light upon this subject, I have endeavoured to eliminate the nitrogen from these compounds by processes likely to act without producing too powerful alterations. The mode of action peculiar to nitrous acid appeared to promise some results; and since indigo, owing to its insolubility, is but little adapted to this reaction, I have made some experiments with isatin, which is so closely allied to indigo.

Supposing isatin to undergo a transformation analogous to that first observed by Piria in similar cases, and consisting arithmetically in the exchange of HN for O, there appeared some hope of obtaining in this manner naphtalic anhydride, and of thus opening a passage from the indigo-group into the naphtalin-series.

Isatin . . .	$C_8H_5NO_2$.
Naphtalic anhydride .	$C_8H_4O_3$.

The history of these two bodies presents some features which conferred a degree of probability on such a transformation. Both isatin and naphtalic anhydride readily assimilate the elements of water, being converted respectively into isatic and naphtalic acids, which, when submitted to the action of alkalies, give both rise to the formation of phenylic derivatives, isatic acid yielding phenylamine, and naphtalic acid being converted into hydride of phenyl (benzol).

Experiment, however, has not confirmed my anticipation, and it might seem superfluous to waste another word upon the subject; nevertheless, I will briefly mention the result of this unsuccessful experiment, since it may probably save some trouble to others.

When studying the deportment of isatin with nitrous acid, I observed the following facts. If finely powdered isatin be suspended in from ten to twenty times its weight of water, and the mixture be then submitted to the action of a current of nitrous acid (disengaged by the action of arsenious acid upon nitric acid, and partially freed from nitric acid by sending it through an empty wash-bottle), the liquid at once begins to effervesce, and the isatin is soon entirely dissolved. The nearly colourless solution invariably contains a considerable quantity of nitric acid generated by the contact of the nitrous acid with the water. To avoid the action of this acid upon the product of the transformation of the

isatin, the liquid, mixed with much water, was evaporated upon the water-bath, the water being repeatedly renewed so as to prevent the nitric acid from getting concentrated. The liquid thus evaporated deposited crystals of an acid which, once or twice recrystallized from boiling water, appeared to be perfectly pure.

On analysis the following numbers were obtained—

I. 0·4308 grm. of the acid gave 0·7203 grm. of carbonic acid, and 0·1094 grm. of water.

II. 0·3164 grm. of the acid gave 0·5306 grm. of carbonic acid, and 0·0874 grm. of water.

These numbers lead to the expression,

$$C_7H_5NO_5 = C_7[H_5(NO_2)]O_3,$$

which is the formula of nitrosalicylic (indigotic) acid.

	Theory.		Experiment. I.	Experiment. II.
C_7	84	45·90	45·60	45·73
H_5	5	2·73	2·81	2·86
N	14	7·65	—	—
O_5	80	43·72	—	—
	183	100·00		

Assuming the nitrosalicylic acid to be a product of oxidation of the body directly formed from isatin under the influence of nitrous acid, the solution before evaporation was neutralized by means of an alkali. The result remained the same. In another experiment, pea-sized pieces of marble were introduced into the mixture of water and isatin before the nitrous acid was passed, in order to remove the free nitric acid as rapidly as it was formed. In these experiments, likewise, nitrosalicylic acid was obtained. It need scarcely be mentioned that the acid derived from isatin possessed all the properties of nitrosalicylic acid prepared by the ordinary method; it exhibited more especially the characteristic coloration with perchloride of iron.

When the liquid obtained by treatment with nitrous acid was evaporated, without having been previously mixed either with water or with an alkali, the isatin, as might have been expected, was transformed into trinitrophenylic acid. This acid was suffi-

ciently characterised by its properties, and by the analysis of its well-known difficultly-soluble potassium-compound.

0·3399 grm. of the potassium-salt, when burnt with chromate of lead, gave 0·3293 grm. of carbonic acid, and 0·0230 grm. of water.

The formula $C_6H_2KN_3O_7 = C_6[H_2(NO_2)_3K]O$ requires the following values,—

	Theory.		Experiment.
C_6	72	26·97	27·14
H_2	2	0·75	0·76
K	39	14·60	—
N_3	42	15·73	—
O_7	112	41·95	—
	267	100·00	

15. *Spontaneous Decomposition of Gun-cotton.*

Some gun-cotton prepared in the establishment of Messrs. Hall, soon after Schönbein's discovery, and taken out of a cartridge intended for blasting, had been preserved by my friend Dr. Percy since 1847, in a glass bottle provided with a glass stopper. After some time, red vapours had appeared in the interior of the bottle, and the cotton had crumbled down to a loose powder. When lately the bottle was again examined, the powder was found to be converted into a light brown, semi-fluid, gum-like mass, while the side of the bottle had become coated with a net-work of fine needles. It was not difficult to collect a sufficient quantity of these crystals; they exhibited all the characters of oxalic acid. In order to fix their nature by a number, they were converted, first into the ammonium-salt, and then into the silver-salt.

0·2420 grm. of silver-salt gave 0·2275 grm. of chloride of silver = 70·74 p.c. of silver.

Oxalate of silver contains 71·05 p.c. of silver.

The viscid mass into which the bulk of the gun-cotton had been converted, exhibited all the properties of ordinary gum; it was likewise interspersed with crystals of oxalic acid.

16. *Experimental illustration of the Composition of Ammonia in Lectures.*

The decomposition of ammonia by the spark-current, exhibits in a conspicuous manner the condensation which accompanies the transformation of a mixture of hydrogen and nitrogen into ammonia. It is more difficult to illustrate the relative proportion of the nitrogen and hydrogen which exists in ammonia. The following experiment elucidates, though indirectly, this relation.

A glass tube from 30 to 40 inches in length, and ¾ of an inch in width, is sealed at one end and divided without particular care into three equal parts, which are conveniently marked by paper or by india-rubber rings. The tube is then filled over water with pure chlorine, and at once transferred into a test-glass half filled with mercury and half with concentrated solution of ammonia. In this manner a layer of ammonia one or two inches in height, and separated from the bulk of the liquid by mercury, is collected in the tube. A lively reaction immediately sets in, the mercury rises, and the ammonia-solution floating on the metal effervesces, with evolution of nitrogen, while the chlorine disappears, dense white clouds of chloride of ammonium being formed.

According to the equation—

$$H_3N + 3Cl = 3HCl + N,$$

the 3 volumes of chlorine should be replaced by 1 volume of nitrogen, and this result is actually observed. At the common temperature, however, the reaction is but slowly accomplished, the disengagement of nitrogen from the solution of ammonia becoming slower and slower, but often continuing for hours. On the other hand, the decomposition is instantaneous if the tube be gently inclined, and the liquid floating upon the mercury be heated to ebullition. To complete the experiment it is only necessary to transfer the glass tube into a high cylinder filled with water, in which the inner and outer liquids may become level when the 3 volumes of chlorine originally filling the tube, are found to be very accurately replaced by 1 volume of nitrogen gas.

Supposing the composition by volume of hydrochloric acid to be known, the composition of ammonia is fixed by this observation. The experiment furnishes moreover an instructive illustration of the volume-equivalence of chlorine, hydrogen, and nitrogen.

17. *How to exhibit the Inflammability of Ammonia.*

It is well known that ammoniacal gas cannot be inflamed in atmospheric air, but will burn in oxygen gas with a greenish-yellow flame. This flame may be shown by allowing the gas to issue from a bent jet into a vessel containing oxygen. There is, however, some difficulty in lighting the gas, and under the most favourable circumstances the phenomenon is very ephemeral. To avoid this inconvenience, the inflammability of ammonia is generally exhibited by sending a current of the gas into an ordinary flame, the ammonia-gas being allowed to issue from the delivery tube into the lower opening of an Argand gas-burner provided with a glass chimney. The gas burning low and almost invisibly, the high lambent ammonia-flame becomes very conspicuous.

The phenomenon may, however, be observed in a purer and much more brilliant form, when a wide-mouthed flask, containing a strong aqueous solution of ammonia is heated upon a sand-bath, and a rapid current of oxygen gas from a gas-holder forced through the boiling liquid. The mixture of oxygen and ammonia-gas thus formed may be lighted, and burns at the mouth of the flask with the characteristic greenish-yellow flame, which continues until the ammonia is expelled from the liquid.

18. *Separation of Cadmium from Copper.*

Having had occasion to perform some experiments on the relative merits of the several processes which have been suggested for the separation of cadmium from copper, I was led to observe a property of sulphide of cadmium, which I do not find noticed in analytical manuals. Sulphide of cadmium dissolves with the greatest facility in boiling dilute sulphuric acid, which has no effect upon the sulphide of copper. On precipitating, by sulphuretted hydrogen, a solution containing not more than 1 milligramme of cadmium mixed with 1000 milligrammes of copper, and boiling the black precipitate for a few seconds with dilute sulphuric acid (1 part of concentrated sulphuric acid and 5 parts of water), a colourless filtrate is obtained, in which an aqueous solution of sulphuretted hydrogen produces an unmistakable precipitate of yellow sulphide of cadmium. Another solution of the same composition was mixed with an excess of cyanide of potassium and treated with sulphuretted hydrogen gas. A distinct yellow

coloration was observed: a deposit likewise took place, but so slowly that in delicacy the former experiment appears to have a considerable advantage, especially since a solution of *pure* copper in cyanide of potassium also gives rise to a yellow coloration, when submitted to the action of sulphuretted hydrogen.

19. *Separation of Arsenic from Antimony.*

The separation of these two metals, which presents unusual difficulties, has been a task of predilection with chemists, and a great number of processes have been suggested, the majority of which, it cannot be denied, admit of improvement. Among the many methods, the one which is based upon the dissimilar deportment of arsenetted and antimonetted hydrogen with nitrate of silver, deserves to be favourably mentioned, the former, as is well known, yielding arsenious acid which passes in solution:

$$H_3As + 6AgNO_3 + 2H_2O = 6HNO_3 + 6Ag + HAsO_2.$$

the latter giving rise to the formation of antimonide of silver:

$$H_3Sb + 3\,AgNO_3 = 3HNO_3 + Ag_3Sb$$

which is insoluble in water. This process presents no difficulty as far as the arsenic is concerned, which may be recognized in solution by ammonia, if there be an excess of silver, or by sulphuretted hydrogen, if the silver has been entirely precipitated. It is far less easy to find, according to this process, minute quantities of antimony in the presence of large quantities of arsenic, the silver-compound of antimony being mixed with a bulky precipitate of metallic silver. By treating this precipitate, as might readily suggest itself, with hydrochloric acid, there dissolves, together with antimony, a small quantity of chloride of silver, which is sufficient to darken the precipitate produced in the solution by sulphuretted hydrogen to such a degree as altogether to mask the presence of antimony. This inconvenience may easily be obviated by boiling the mixture of silver and antimonide of silver, after the arsenious acid has been carefully washed out by boiling water, with *tartaric acid,* which dissolves the antimony alone. The solution thus obtained yields at once the characteristic orange-yellow precipitate with sulphuretted hydrogen.

In some experiments made with the view of testing the delicacy of this process, 1 part of antimony in presence of 199 parts of arsenic, and *vice versâ,* 1 part of arsenic, together with 199 parts

of antimony, could be easily detected. Even with minute quantities the process proved successful, inasmuch as 5 milligrammes of either metal in the presence of 100 times the amount of the other could be satisfactorily exhibited. In evolving the hydrogen-compounds of arsenic and antimony, care must be taken to add as little nitric acid as possible to the hydrochloric acid used in dissolving the sulphides of the metals, since the presence of even moderate quantities of this acid greatly interferes with the free disengagement of the gases.

If there be tin with the arsenic and antimony, this metal will be deposited upon the plates of zinc used in evolving the hydrogen, from which it may be mechanically detached, dissolved in hydrochloric acid, and tested by the usual processes.

20. *Analysis of the Saline Water of Christian Malford, near Chippenham.*

The water used for analysis, was collected November 11, 1858.

The water pumped up from the well is perfectly clear and colourless, and almost inodorous. It has a distinctly saline taste, and effervesces on agitation, exhibiting the presence of a considerable quantity of free carbonic acid. The water contains, in addition to carbonic acid, a minute trace of an inflammable carbonetted hydrogen. The presence of the latter becomes perceptible if a considerable quantity of the water be heated to ebullition, and the gases expelled be passed through a solution of potassa. The gas not absorbed is a mixture of atmospheric air with the carbonetted hydrogen; it burns, owing to the preponderance of the air, with a pale scarcely visible flame. On standing, more readily on boiling, the water deposits a yellowish sediment, consisting of carbonate of calcium, carbonate of magnesium, sesquioxide of iron, and organic matter.

Temperature of the water 12°C, the temperature of the air being nearly the same.

Specific gravity of the water = 1·006.

The analysis was performed in the usual manner; only the determination of the bromine requires a passing notice.

In determining this element, I have availed myself of the method of imperfect precipitation. According to the observations of Lyte and of Field, nitrate of silver produces in a mixture of chloride, bromide, and iodide, a precipitate, first of

iodide, and then of bromide, and a precipitate of chloride only after the whole of the iodine and bromine have been separated ;— a method of separating chlorine, bromine, and iodine, based upon this deportment, has been proposed by the latter chemist.

The amount of iodine present in the water of Christian Malford, is so exceedingly small, that the quantitative determination appeared useless. The task was, therefore, limited to the determination of the bromine.

For this purpose, 28 litres of the water were evaporated to dryness, and the saline residue was exhausted with dilute alcohol. The alcoholic liquid, when submitted to distillation, left a saline mass, which was dissolved in a small quantity of water. This solution was measured and divided into two equal parts, each of which represented the extract of the saline residue of 14 litres = 14084 grammes of the original water, containing the whole of the bromides and part of the chlorides. Each of the liquids thus obtained was precipitated by a silver-solution, containing 0·4288 grammes of pure silver, whereby the whole of the bromine, and part of the chlorine was thrown down. The two precipitates weighed respectively 0·6355 (I), and 0·6350 (II) grammes.

If P represent the weight of the mixed precipitate, and x the amount of chloride of silver in it, then $P-x$ is the quantity of bromide of silver, and if the total amount of the silver in the precipitate be represented by S, then

$$S = \frac{108}{143{\cdot}5} x + \frac{108}{188} (P - x)$$

whence

$$x = \frac{S - 0{\cdot}5745\, P}{0{\cdot}1781}.$$

By substituting the experimental values for S and P in the above expression, we find

	I.	II.
Chloride and bromide of silver (by experiment)	0·6355	0·6350
Chloride of silver (by calculation)	0·3576	0·3593
Bromide of silver	0·2779	0·2757
Corresponding (in 14084 grms. of water) to bromine . . .	0·1182	0·1173
Or in 1000 grms. to	0·0084	0·0083

Direct results of analysis calculated to 1000 grammes of water.

a. Bases.

Experiment.	Sesquioxide of Iron.	Lime.	Magnesia.	Alkaline Chlorides.	Chloride of Potassium.	Chloride of Sodium.
I.	0·0035	0·4234	0·1897	6·9600	0·863	6·097
II.	0·0035	0·4241	0·1903	6·8800	0·897	5·983
Mean....	0·0035	0·4238	0·1900	6·9200	0·880	6·040

b. Acids
(*or elements replacing them*).

Exp.	Sulphuric Acid.	Chlorine.	Bromine, with traces of Iodine.	Silica.	Carbonic Acid free and combined.	Carbonic Acid combined as Carbonate of Calcium and Magnesium.	Carbonic Acid free.
I.	0·2464	4·5630	0·0084	0·0150	0·2921	0·1050	0 1871
II.	0·2452	4·5570	0·0083	0·0145	0·3164	0·1072	0 2092
Mean ..	0·2458	4·5600	0·0084	0·0148	0·3043	0·1061	0·1982

c. Residue left on Evaporation.

Experiment.	Mineral Residue.	Organic Matter.	Total Residue.
I.	8·2000	0·0200	8·2200
II.	8·1900	0·0200	8·2100
Mean	8·1950	0·0200	8·2150

VERIFICATIONS.

a. Verification for Lime.

Experiment.	Lime precipitated on ebullition. (Carbonate of Calcium.)	Lime left in solution after ebullition. (Sulphate and Chloride of Calcium.)	Total by Calculation.	Total by Experiment
I.	0·1285	0·2895	0·4180	0·4234
II.	0·1307	0·2856	0·4163	0·4241
Mean	0·1296	0·2876	0·4172	0·4238

b. Verification for Magnesia.

Experiment.	Magnesia precipitated on ebullition. (Carbonate of Magnesium.)	Magnesia left in solution after ebullition. (Chloride of Magnesium.)	Total by Calculation.	Total by Experiment.
I.	0·0022	0·1852	0·1874	0·1897
II.	0·0025	0·1863	0·1888	0·1903
Mean	0·0024	0·1857	0·1881	0·1900

Saline Constituents.

	In 1000 grammes of water.	In one gallon, (70,000 grains) of water.
	Grammes.	Grains.
Sulphate of calcium . . .	0·4179	29·253
Carbonate of calcium . . .	0·2314	16·198
Chloride of calcium . . .	0·2289	16·023
Carbonate of magnesium . .	0·0050	0·350
Chloride of magnesium . .	0·4413	30·891
Bromide of magnesium (with traces of iodide of magnesium)	0·0096	0·672
Carbonate of iron . . .	0·0051	0·357
Chloride of potassium . .	0·8800	61·600
Chloride of sodium . . .	6·0400	422·800
Silica	0·0148	1·036
Organic matter	0 0200	1·400
	8·2940	580·580

The water contains 29·02 cubic inches in the gallon, or 104·6 cubic centimetres in the litre, of free carbonic acid. The quantity of carbonic acid was determined at the well. It deserves to be mentioned that the water for this purpose was pumped up, whereby probably a minute quantity of gas was lost.

My thanks are due to Mr. E. Millar, of Christian Malford, for his help in collecting the water, and to Dr. Leibius for his assistance in performing the experiments.

21. *Spontaneous Decomposition of Chloride of Lime.*

One morning (I think it was in the summer of 1858), when entering my laboratory, which I had left in perfect order on the previous evening, I was surprised to find the room in the greatest confusion. Broken bottles and fragments of apparatus lay about, several window panes were smashed, and all the tables and shelves were covered with a dense layer of white dust. The latter was soon found to be chloride of lime, and furnished without difficulty the explanation of this strange appearance.

At the conclusion of the Great Exhibition of 1851, M. Kuhlmann, of Lille, had made me a present of the splendid collection of chemical preparations which he had contributed. The beautiful large bottles were for a long time kept as a collection; gradually, however, their contents proved too great a temptation, and in the course of time all the substances had been consumed. Only one large bottle, of about 10 litres capacity, and filled with chloride of lime, had resisted all attacks; the stopper had stuck so fast that nobody could get it out; and after many unsuccessful efforts—no one venturing to indulge in strong measures with the handsome vessel—the bottle had at last found a place on one of the highest shelves of the laboratory, where for years it had remained lost in dust and oblivion, until it had forced itself back on our recollection by so energetic an appeal. The explosion had been so violent that the neck of the bottle was projected into the area, where it was found with the stopper still firmly cemented into it.

I have not been able to learn whether similar cases of the spontaneous decomposition of chloride of lime have been already observed.

22. *Bisulphide of Carbon in Coal Gas.*

It is well known that coal gas, even when submitted to the most improved processes of purification, retains a minute quantity of a sulphur-compound, which yields sulphurous acid when the gas is burned. A commission having been appointed for the purpose of reporting* to the Lords of the Committee of Privy Council on Education on the lighting of picture-galleries by gas, and on any precautions (if necessary) against the escape of gas and of the products of its combustion, the writer of this note undertook a few experiments, with the view of determining the amount of sulphur generally present in the London coal gas.

The object of the inquiry being to ascertain the quantity of sulphurous acid capable of being formed by the combustion of the gas, an exceedingly small jet of gas, carefully washed with acetate of lead—which showed the absence of sulphuretted hydrogen—and measured by an accurate experimental meter, was burned in a large two-necked glass globe. Through one of the necks the gas tube was conveyed into the globe, whilst the other, fitting into a condenser, carried off the product of combustion into a two-necked receiver. To establish a current of air, the receiver was connected with a water-current aspirator, a couple of Woolfe's bottles containing water or dilute ammonia being inserted, for the purpose of fixing any trace of sulphurous acid which might escape condensation, with the water, in the receiver. The experiment being terminated, the liquids in the receiver and in the wash-bottles were united, oxidized with chlorine and precipitated with chloride of barium.

Experiments in July, 1859.

Order of Experiments.	Quantity of Gas consumed.	Amount of Sulphate of Barium.	Amount of Sulphur in 100 cubic feet.		Amount of Sulphur in 100 cubic metres.
	Cubic feet.	Grammes.	Grammes.	Grains.	Grammes.
I.	1·98	0·0630	0·437	6·74	15·433
II.	2	0·0840	0·577	8·90	20·371
III.	2	0·0630	0·433	6·68	15·278
IV.	2	0·0740	0·508	7·84	17·944
Mean	..	..	0·488	7·54	17·256

* Report on the subject of Lighting Picture Galleries by Gas, by Professors Faraday, Hofmann, and Tyndall, Mr. Redgrave, R.A, and Capt. Fowke, R.E,

Experiments in December, 1859, and January, 1860.

Order of Experiments.	Quantity of Gas consumed. — Cubic feet.	Amount of Sulphate of Barium. — Grammes.	Amount of Sulphur in 100 cubic feet. Grammes.	Amount of Sulphur in 100 cubic feet. Grains.	Amount of Sulphur in 100 cubic metres. — Grammes.
V.	2	0·0890	0·611	9·43	21·585
VI.	2	0·0953	0·654	10·10	23·111
VII.	2	0·0975	0·669	10·33	23·644
VIII.	2	0·0935	0·642	9·91	22·677
Mean	..	..	0·644	9·94	22·754

These experiments show that the amount of sulphur remaining in the London gas after the removal of the sulphuretted hydrogen is very small, and that in winter it is somewhat greater than in summer. This may possibly arise from the enormously increased production of gas during the winter months, when it will be more difficult to regulate the several processes involved in its manufacture. But the result may also be purely accidental, arising from a change in the nature of the coal used, etc. A much more extended series of experiments would be required to decide this question.

It has long been assumed that the sulphur in purified gas exists in the form of bisulphide of carbon, the conditions for the generation of this compound being in fact given in the ordinary process of producing gas. That coal gas really contains bisulphide of carbon was first elegantly proved by Vogel,* who, at the suggestion of Baron Liebig, passed a current of purified gas through an alcoholic solution of potassa, when xanthate (sulphocarbonate) of potassium ($K(C_2H_5)CS_2O$) was formed, which produced in copper-solutions the highly characteristic yellow precipitate of xanthate of copper, and yielded, when boiled with a few drops of nitrate of lead in the presence of free potassa, a black deposit of sulphide of lead. When engaged in the above inquiry, I repeated Vogel's experiments, which I can confirm in every particular. The amount of bisulphide of carbon in the London gas is, however, so small, that a very large volume must be passed through the alcoholic solution of potassa in order to produce a sufficient quantity of xanthate of potassium. After a cubic foot of gas had been passed through alcoholic potassa in a bulb apparatus, the

* Liebig's Annalen lxxxviii, 369.

solution gave with sulphate of copper a leek-green precipitate, in which the presence of xanthate was but imperfectly indicated. Only after passing several additional cubic feet the yellow colour became more distinct, although still masked to some extent by the hydrated protoxyde simultaneously precipitated. On the other hand, the black precipitate of sulphide of lead was obtained without difficulty, even after the passage of one single cubic foot of gas.

But the presence of bisulphide of carbon in coal gas may be exhibited even more elegantly, and with greater precision, by means of *triethylphosphine*, which produces with the bisulphide a compound crystallizing in splendid prisms of a ruby colour. This body is so characteristic, and forms with so much facility, that bisulphide of carbon has become a most valuable re-agent for triethylphosphine and its homologues. The idea naturally suggested itself to employ the phosphorous-base for the detection of bisulphide of carbon in gas. On distilling a considerable proportion of coal-gas-benzol, I had separately collected a small fraction, which came over in the commencement below 65°. When mixed with triethylphosphine, this liquid solidified into a mass of the well known ruby crystals. Four or five drops of triethylphosphine were dissolved in ether, the ethereal liquid was introduced into a bulb apparatus, and a current of coal gas allowed to bubble through the solution. When 0·2 of a cubic foot had passed, the liquid had assumed a distinctly red coloration, the intensity of which increased as the passage of the gas and the evaporation of the ether continued. After 0·8 of a cubic foot had passed, the whole of the ether had evaporated, and the inner surface of the bulb-apparatus was lined with a beautiful network of the ruby crystals.

23. *Remarks on the Changes of Gutta Percha under Tropical Influences.*

[From a Report addressed to Sir W. B. O'Shaughnessy, Director-General of Telegraphs in India.]

The peculiar change which gutta percha undergoes when in contact with air for some time is well known, this substance gradually becoming brittle, and ultimately losing all coherence. This effect was experienced on an undesirable scale in construct-

ing the East Indian Telegraphs. Enormous quantities of gutta percha, became in a comparatively short time, entirely useless, involving a loss of thousands of pounds. At the request of Sir W. B. O'Shaughnessy I have made a few experiments with the gutta percha thus altered, the results of which were recalled to my mind by the researches on the alteration of gutta percha lately published by Oudeman. It may be of some interest briefly to mention the analytical results furnished by the changed material submitted to me for examination.

The specimens sent home from India formed a brown, exceedingly brittle substance, softening to a plastic mass in boiling water. Since the gutta percha existing in commerce does not always exhibit the same characters, it was of some importance for the inquiry, that a quantity of the original unchanged substance, with which the wires sent out to India had been coated, was likewise placed at my disposal. In their deportment with solvents the changed and unchanged gutta percha exhibited a marked difference. Whilst the latter proved to be perfectly insoluble in strong alcohol, the changed gutta percha was in a great measure taken up by this solvent. By treating the changed material first with cold, then with boiling alcohol, and ultimately with ether, three substances were obtained, which, although very much alike in their physical properties, differed considerably from each other in their chemical composition.

I.—*Substance soluble in cold Alcohol.*

Cold alcohol readily attacked the outer surface of the coating, and dissolved a considerable portion. On evaporation a brown resinous mass remained behind, which was dried, first over sulphuric acid, and ultimately at 100°; at which temperature it readily fused. The fused mass solidified on cooling to a brittle substance, yielding a highly electrical powder, and exhibiting on combustion the following percentage composition.

	I.	II.	Mean.
Carbon	62·94	62·64	62·79
Hydrogen . . .	9·22	9·36	9·29
Oxygen	27·84	28·00	27·92
	100·00	100·00	100·00

II.—*Substance soluble in boiling Alcohol.*

By treating with boiling alcohol the residue of the previous operation, which had ceased to yield anything more to cold alcohol, a fresh quantity of substance was obtained in solution. The alcoholic liquid, on evaporation, left a residue very similar to that of the previous operation, which, when dried in the same manner, furnished on analysis the following numbers.

	I.	II.	Mean.
Carbon	68·13	67·29	67·72
Hydrogen . . .	10·01	10·18	10·09
Oxygen	21·86	22·53	22·19
	100·00	100·00	100·00

III.—*Substance insoluble in cold and in boiling Alcohol.*

The residue left after repeated treatment with boiling alcohol, dissolved in ether, a few mechanical impurities remaining behind. The ethereal solution gave with alcohol a precipitate which dried up to a yellowish powder, becoming highly electrical by trituration, and caking when gently heated. It had the general characters of gutta percha, being merely somewhat deeper coloured and less plastic. When analysed, it furnished numbers nearly agreeing with those which were obtained by several observers for gutta percha.

Carbon	88·12
Hydrogen	12·19

The body last analysed was obviously unchanged gutta percha; a view which is also supported by its solubility in chloroform and benzol. The substance in question differed from specimens of gutta percha investigated by others, and especially from that which Payen considers the pure gutta percha, by its solubility in ether. The original substance with which the wires had been coated was, however, likewise soluble in ether. It cannot, therefore, be doubted that gutta percha exists in several modifications.

The experiments which I have quoted prove that the changes which gutta percha undergoes in contact with air depend upon oxidation. Unchanged gutta percha is free from oxygen; the product dissolved by cold alcohol contained nearly 28 per cent.,

and that soluble in boiling alcohol still more than 22 per cent. of oxygen.

I need not mention that I am far from believing that these oxygenated substances are definite chemical compounds. Their mode of preparation altogether precludes such an idea, the object of the experiments having been simply to establish the fact of oxidation having taken place. That the changes of gutta percha are due to the absorption of oxygen, is countenanced by the experience of this substance having been kept for years under water without undergoing any alteration.

On the Carbonates of Alumina, Ferric Oxide, and Chromic Oxide.

By James Barratt, Esq.

(*Abstract.*)*

The composition of the precipitate produced in solutions of sulphate or chloride of aluminium by alkaline carbonates has been variously stated as follows :—According to

Muspratt (Chem. Soc. Qu. J. ii. 216),	it is	$3Al_2O_3 . 2CO_2 + 4HO$
H. Rose (Pogg. Ann. xci. 452)	„	$Al_2O_3 . 3HO + NH_4.CO_2 + HO$
Langlois (Ann. Ch. Phys. [3] xlviii. 502)	„	$8Al_2O_3 . CO_2 + 8HO$
Wallace (Chem. Gaz. 1858, 410)	„	$3Al_2 . 2CO_2 + 9HO$

From experiments made by the author of this paper in Dr. Muspratt's laboratory, it appears that the precipitate formed by carbonate of soda in a solution of chloride of aluminium (the mode of preparation adopted by Wallace), after being washed and dried, then triturated with water, again washed, and dried over sulphuric acid, consists of hydrate of alumina perfectly free from carbonic acid, a result which agrees with the statement of Saussure (Gmelin's Handbook, iii. 308.)

Carbonate of Chromic Oxide has been analysed by several chemists. According to

Berzelius (Traité, iv., 427),	it is	$4Cr_2O_3 . CO_2 + 3HO$
Meissner (Gilb. Ann. lx. 366)	„	$10Cr_2O_3 . 7CO_2 + 8HO$
Langlois (loc. cit.)	„	$2Cr_2O_3 . CO_2 + 6HO$
Lefort (Compt. rend. xxvii. 269) } Wallace (loc. cit.) }	„	$Cr_2O_3 . CO_2 + 4HO$

* This paper is published *in full* in the Chemical News, No. 10, p. 110.

Mr. Barratt's experiments confirm the result obtained by Lefort and Wallace.

Carbonate of Ferric Oxide.—Soubeiran (Ann. Ch. Phys. [2] xliv. 326) found that the precipitate thrown down by alkaline carbonates from *ferrous* salts, after thorough washing and exposure to the moist air of a cellar for six months, no longer contains ferrous oxide, but consists of 71·4 p.c. Fe_2O_3, 8·3 CO_2 and 20·0 water ($3Fe_2O_3.CO_2+12HO$). According to Langlois (loc. cit.), the precipitate formed by alkaline carbonates in ferric salts, contains, when dried at 100° C., 81·17 p.c. Fe_2O_3, 10·17 HO and 1·36 CO_2, which is given off at 165°. L. Gmelin (Handb. v. 222), on the contrary, states that this precipitate, after thorough washing, is quite free from carbonic acid. According to Wallace (loc. cit.), the precipitate thrown down by carbonate of ammonia from ferric chloride, contains, when dried in the air at 22° to 24° C., $3Fe_2O_3.CO_2+6HO$, and gives off 2 eq. water at 100°; and the precipitate formed by carbonate of soda in a solution of ferric nitrate is $9Fe_2O_3.CO_2+12HO$.

Mr. Barratt finds that the precipitate dried in the air at ordinary temperatures contains $3Fe_2O_3.CO_2+8HO$, half of the water being expelled at 100° C.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

January 19, 1860.

Professor Brodie, President, in the Chair.

The following were elected Fellows of the Society:—

Charles A. Cameron, M.D., Dublin; Charles Henry Wood, Esq., 17, Bloomsbury-square; August Dupré, Ph.D., 53, Burton-crescent; William Plunket, Esq., Museum of Irish Industry, Dublin.

The following papers were read:—

"On refining Gold when alloyed with Tin or Antimony, so as to render it fit for the purposes of coinage," by Mr. Robert Warrington.

"On certain sources of loss of precious Metal in some operations of assaying," by Mr. G. H. Makins.

"On the double Sulphides of Iron and Copper," by Mr. F. Field.

February 2, 1860.

Dr. H. Bence Jones, Vice-President, in the Chair.

Edward Divers, Esq., Queen's College, Galway, and Edwin Crocker, Esq., 19, Richmond-road, Barnsbury, were elected Fellows of the Society.

The following papers were read:—

"On an Iron Sand from New Zealand," by Dr. J. H. Gladstone.

"On the composition of Air from Mont Blanc," by Dr. E. Frankland.

"On Biniodacetic Acid," by Messrs. Perkin and Duppa.

February 16, 1860.

Professor Brodie, President, in the Chair.

The following were elected Fellows of the Society:—

Frederick Dupré, Ph.D., 53, Burton-crescent; Dr. Edward Smith, 6, Queen Ann-street, Cavendish-square; Edward Nicholson, Esq., St. Mary's Hospital, Paddington.

A paper was read "On some derivatives from the Olefines," by Dr. Guthrie.

Dr. Odling made a verbal communication "On the direct Oxidation of Chlorhydric Acid."

March 1, 1860.

Dr. W. A. Miller, Vice-President, in the Chair.

Messrs. Berthelot, Deville, Frémy, Fritzsche, Peligot, and Mulder, were elected Foreign Members.

George Morley, Esq., 18, Park-place, Leeds, was elected a Fellow of the Society.

The following papers were read:—

"On New Zealand Iron Sand," by Mr. E. Riley.

"On the action of Chloride of Ethyl upon Ammonia," by Mr. Groves.

March 15, 1860.

Dr. W. A. Miller, Vice-President, in the Chair.

The following papers were read:—

"On the composition of the Platinidcyanides," by Mr. Hadow.

"On a new Ammonio-chrome Compound," by Mr. Morland.

"On the analysis of a Water from the superficial strata of the London basin," by Mr. Hooker.

Anniversary Meeting, March 30, 1860.

Professor Brodie, President, in the Chair.

The Report of the Council, and the Audited Account of the Treasurer, were read.

Messrs. Crookes and Morland having been appointed Scrutators, the Meeting proceeded to the election of Council and Officers for the ensuing year, and the following were declared to have been duly elected:—

President.—B. C. Brodie, F.R.S.

Vice-Presidents, who have filled the office of President.—W. T. Brande, F.R.S.; C. G. B. Daubeny, M.D., F.R.S.; Thomas Graham, F.R.S.; W. A. Miller, M.D., F.R.S.; Lyon Playfair, Ph.D., F.R.S.; Colonel Philip Yorke, F.R.S.

Vice-Presidents.—E. Frankland, Ph.D., F.R.S.; H. Bence Jones, M.D., F.R.S.; Robert Porrett, F.R.S.; Alfred Smee, F.R.S.

Secretaries. — Theophilus Redwood, Ph.D.; William Odling, M.B., F.R.S.

Foreign Secretary.—A. W. Hofmann, LL.D., F.R.S.

Treasurer.—Warren De La Rue, Ph.D., F.R.S.

Other Members of Council.—Frederick Field; William Francis, Ph.D., F.L.S.; G. D. Longstaff, M.D.; Dr. Marcet, F.R.S.; John Mercer, F.R.S.; Henry M. Noad, Ph.D., F.R.S.; A. R. Normandy, A.R.L.M.; H. E. Roscoe, Ph.D.; Edward Schunck, Ph.D.; J. A. Voelcker, Ph.D.; Robert Warington; A. W. Williamson, Ph.D.; F.R.S.

It was resolved—

That the thanks of the Meeting be given to the President, Officers, and Council, for their services during the past year.

That the thanks of the Meeting be given the Auditors for their services to the Society.

The following donations have been received :—

"Repertory of Arts and Manufactures :"
"Repertory of Patent Inventions :"
"London Journal of Patent Inventions :"
Carpmael's "Law of Patents of Invention :"
Carpmael's "Law Reports of Patent Cases :"
from Messrs. De La Rue and Co.

"Quarterly Journal of the Geological Society," Part 1, for 1860 : from the Society.

"Pharmaceutical Journal" for January, February, March, 1860 : from the Editors.

"Chemical News," Nos. 1 to 16 : from the Publishers.

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IX.—*On certain sources of loss of Precious Metal in some operations of Assaying.*

By G. H. Makins.

In the assay of specimens of alloyed gold, the degree of heat used in the first operation, viz., cupellation (when this is carefully performed), is usually somewhat varied, according to presupposed proportions in the alloy,—for example, a much lower temperature being sufficient where the gold is only associated with silver, than where it is also mixed with oxidisable metals, which latter have to be separated entirely by this first operation.

About five years since, I chanced to have before me some 200 assays of gold, wherein the silver also had to be estimated, and in which, for other reasons, an extraordinary degree of heat was required to be employed; and as I made simultaneously with these, several synthetical proofs, I was much struck by the great extent of loss of gold and silver; and satisfied that it could not be entirely due to what is known amongst assayers as cupel absorption, I determined upon examining some of the contents of an iron flue of a cupel furnace, which passed from its hood into a chimney, in order to see if gold had been volatilized along with other metals, and if so, to what extent.

A quantity of apparently carbonaceous matter was therefore taken out of it; and as this flue was at the time recently put up afresh, I had the means of knowing that it had been used for the cupellation of gold assays only.

Upon examination of this material by the microscope under an inch power, it exhibited very distinctly portions of oxide of lead, in yellow masses, little nodules of suboxide of copper, minute grains of silver, together with portions resembling silver reduced from chloride,—the whole mixed with a quantity of carbonized matter containing small grains of unburnt fuel.

From pressure of business at the time, this material was laid aside (after cursory examination sufficient to prove the presence of the metals), until it could be completely examined. This was not done, however, until after the appearance of some collateral matter, communicated to the Society by my late pupil, Mr. Napier.

On further examination, the metallic matters present were found to consist of oxide of lead mixed with small portions of gold, silver, and oxide of copper; and as my object was only to estimate the gold and silver present, I took separate portions, viz., two of 50, and two of 100 grains each. They were each treated with 400 grains of pure lead, that is to say, with eight times the weight of the former two, and four times the latter, each having also its own weight of borax added.

The mixtures were then scorified, and the operation carried to its full extent, so as to diminish as much as possible the quantity of lead for the subsequent cupel process.

The process completed, the specimens were poured in a good fluid condition; the slag (which was quite free from metallic beads) separated; and the resulting metal next subjected to cupellation.

The little buttons so obtained, consisting of pure silver and gold, were then weighed.

From the first two assays (the material operated upon being 100 grains), the resulting buttons weighed (after compensating for silver contained in the lead employed), just ·089 grain.

From the second two, upon 200 grains, the buttons weighed ·166. If we average these, which are very nearly alike, and calculate the quantity for 1000 grains, we should have a result of ·850 grain.

They were next all parted for gold, and the result was ·026; equal to ·087 in every 1000 grains.

Deducting then the weight of this gold from the weight of the compound metal, we find the quantity of the precious metals in 1000 grains to be,

Gold ..	·087
Silver ..	·763

Of course I do not attempt to establish any ratio between these quantities and an individual assay; for although the flue whence this material was taken had only been renewed a few months, yet during that time the fumes of many thousand assays had passed through it. But, on the other hand, I would remark, that considering that this flue is removed daily when the furnace is at work, the proportion which the precious metals bear to the whole, is very large indeed.

I will now call attention to a second cause of loss of gold occurring in parting operations, and possibly also in refining upon the large scale, viz., the solution of a portion of gold in the nitric acid used, although the latter is pure and quite free from hydrochloric acid.

Berzelius, in speaking of this fact says, "It must not be forgotten that if nitric acid contains hydrochloric or *nitrous* acid, it will dissolve gold; in truth, the quantity dissolved is inconsiderable in the latter case, but sufficient to lead to an incorrect result." Now, in parting gold by nitric acid, we are generating during the operation quantities of nitrous acid, and consequently have the conditions present for this loss to take place.

Some time since, Mr. Field (the Queen's Assay Master), had in his office a pear-shaped bottle, into which nitric acid was constantly being poured after parting operations: it was thickly coated with gold. He showed this to Sir J. Herschell, who was then Master of the Mint, asserting that it was deposited from an actual solution of the gold. The latter gentleman supposed rather that it was a deposit from mechanically suspended particles; but this could have hardly been the case, as the bottle was a large pear-shaped one, and the gold coated the upper part as thickly as the lower, and very uniformly, which certainly could not have been the case had it been simply a deposit of mechanically suspended particles. It was no doubt, as Mr. Field observed, a good example of deposit from an actual solution.

I tried the following experiment, in order to arrive at some idea of the quantity so taken up in ordinary assaying operations.

Four assay-quantities of pure gold were accurately weighed, then added to the usual proportion of fine silver, and of lead, and cupelled. The buttons then rolled and coiled, were parted with nitric acid. For the boilings, acids were prepared of specific gravity 1·25 and 1·35 respectively.

No. 1 assay was then boiled 20 minutes in the weaker, and afterwards for 13 minutes in the stronger acid, between which operations the cornet was washed with hot distilled water.

No. 2 assay was boiled once in the first, and twice in the second acid.

No. 3. Once in the first, and three times in the second.

And No. 4. Once in the first, and four times in the second; the boilings, as I have said, being continued for 20 minutes in the weak, and for 13 minutes in the second acid.

The several cornets were then washed off with hot distilled water, annealed, and weighed, and the following is the result:—

Calling the weighings before the operations 1000: the first cornet weighed 999·6, the second 992, the third 998·7, and the fourth, 997·9; the loss thus increasing in proportion as we multiply the number of boilings.

Now, the question occurs as to whence the loss arises. I may first say, that it has been suggested that it is due to silver being more completely separated by the repeated boilings.

But in reply to this I can state, that I have examined these cornets over and over again; and that after the first boiling as above described, the amount of silver left in them is very uniformly 1·16 in the 1000 parts. But the difference between 999·6, the weight of the first cornet, and 997·9, that of the fourth, is 1·70; here then, supposing the latter to be entirely free from silver (which is not really the case), we have 0·54 abstracted, a quantity just equal to 3 grains in the troy pound, which loss can only be traced to the removal of gold.

Next: it has been urged, that the appearance of gold in the used parting acid, is due to mechanical causes, dependent upon the friction of an exceedingly soft and spongy body, by its being thrown violently about in a dense acid fluid, and by the rapid evolution of bubbles of acid, or acid vapour, rushing from its surface, all this being of course increased as the density of the acid is increased by evaporation.

I believe that this is not the case, and that in the fluid medium no such abrasion takes place, but that it is a true case of solution,

and by the agency of the nitrous acid evolved. In proof of this I have taken a portion of this acid which had been so used, and after dilution, separated the silver, then evaporated, and obtained small quantities of gold, which were next redissolved in nitro-hydrochloric acid, and proved to be such by the usual tests.

Again, I do not think that the deposit upon Mr. Field's store bottles (to which I have alluded), could have taken place in so regular a manner upon their upper portions without actual solution; for had it been mere mechanical suspension, the metal upon the lower part would of course have been much in excess.

Now, as to the evolution of this nitrous acid. At the first boiling, when the silver is present in such large quantity, nitrous acid is given off most copiously; but probably its solvent action upon the gold is then controlled and checked by electrical action, that is, by the gold becoming the negative, and the silver the positive element in a voltaic circuit; but when the silver is wholly (or nearly) removed, this check no longer exists, and the solution of the gold progresses more rapidly.

Then, with respect to the cause of the evolution of nitrous acid,—of course as I have already said, as long as there is any silver to oxidise, it will be generated; and when the silver is nearly abstracted, the method of boiling adopted by many assayers induces its continuance; for it is scarcely possible to boil an assay in strong acid without some means of disengaging the vapour formed; if some help be not afforded, the acid will "bump" so much as almost, if not quite, to throw it out of the flask. Hence it is the custom with some to introduce a small portion of charcoal, which, from its porosity, tends to the steady evolution of this vapour. Now, if the charcoal be entirely carbonized, it does not materially affect the acid; but if it contain much woody matter not thoroughly carbonized, it is then sure to decompose it, and set nitrous acid free. Indeed, I have for some years ceased to use this body, from its injurious effects upon the acid.

I am aware that the matters mentioned in this paper are somewhat trivial in a scientific point of view; but their commercial importance will be at once admitted, when we remember the enormous values dealt with in this country, and consider, moreover, that they are at times turned over and over again and that

the question of profit and loss in such commercial operations are much, if not entirely, in the hands of the assayer.

Lastly, this publication may serve to account for some of the discrepancies which are sometimes found between assayers.

X.—*On Bibromosuccinic Acid and the Artificial Production of Tartaric Acid.*

By W. H. Perkin, F.C.S., and B. F. Duppa, Esq.

In April of last year, we published a paper on the action of pentachloride of phosphorus on malic acid,* in which we stated that there seemed reasons for believing that there existed a close relation between succinic, malic, and tartaric acids, similar to that which exists between acetic, glycollic, and glyoxylic acids; and for the purpose of verifying that supposition, we proposed endeavouring to obtain mono- and bibromo-succinic acids, thinking that by hydrating them by means of hydrate of silver, or by decomposing their silver-salts in the presence of water, we might obtain malic and tartaric acids. Since that time, we have obtained both of these bromo-acids, but up to the present have only studied the bibromosuccinic acid.

Bibromosuccinic Acid.

We endeavoured to produce this substance by the direct action of bromine on succinic acid, but did not obtain any satisfactory results. The process by which we have succeeded in obtaining this acid, is as follows:

Equal volumes of bromine and chloride of succinyl are heated in a strong sealed tube to a temperature of 120 or 130°C. for three or four hours. The tube, after having cooled, must be very carefully opened, so that the hydrobromic acid which has formed may slowly issue forth; if the tube be opened too rapidly, its contents will be projected and lost. The product thus obtained is an oily liquid consisting of impure chloride of bibromosuccinyl. This is

* Phil. Mag. April 1859.

decomposed by being well agitated for an hour or two with two or three times its volume of water, after which, the liquid will contain considerable quantities of the new acid in the form of a crystalline precipitate; this is purified by being well washed on a filter to separate hydrochloric acid, and also another extremely soluble acid which has been formed. It is then dissolved in a moderately strong solution of carbonate of sodium and filtered for the purpose of removing a small quantity of an oily substance. The resulting sodium salt is then decomposed by nitric acid, which causes the new product to separate as a crystalline precipitate, which, when thoroughly washed on a filter with cold water and then dried, constitutes pure bibromosuccinic acid.

Carbon, hydrogen, and bromine determinations of specimens dried in vacuo over sulphuric acid, gave the following numbers:—

I. ·4150 of substance, gave
·2643 of carbonic acid and
·0600 of water.

II. ·2950 of substance, gave
·4035 of bromide of silver.

Percentage composition:—

	I.	II.
Carbon . .	17·36	—
Hydrogen .	1·60	—
Bromine . .	—	58·2

which agree with the formula,

$$C_8 \left\{ \begin{matrix} H_4 \\ Br_2 \end{matrix} \right\} O_8$$

as may be seen from the following table:—

		Theory.		Experiment.
Carbon	8 equiv. . .	48	17·39	17·36
Hydrogen	4 „ . .	4	1·44	1·60
Bromine	2 „ . .	160	57·97	58·20
Oxygen	8 „ . .	64	23·20	——
		276	100·00	

Bibromosuccinic acid is difficultly soluble in cold, but tolerably so in hot water, from which it crystallises on cooling in opaque

prisms; it is very soluble in alcohol and extremely so in ether. We have found the latter solvent very useful in separating small quantities of this acid from its aqueous solutions. Crystals of bibromacetic acid decrepitate when gently heated, but when subjected to a high temperature, decompose with formation of hydrobromic acid. It has a strong acid taste and reddens litmus rapidly. We have but cursorily examined the salts of this acid.

Bibromosuccinate of sodium is very soluble and appears to contain water of crystallisation.

Acid *bibromosuccinate of potassium* is a white crystalline salt sparingly soluble.

Bibromosuccinate of silver is obtained by adding a solution of nitrate of silver to either of the above salts. It is a white salt nearly insoluble in water. The following determinations were made of a specimen dried over sulphuric acid in vacuo :—

I. ·5316 of substance, gave
·1879 of carbonic acid and
·0288 of water.

II. ·4163 of substance, gave
·2418 of chloride of silver and
·3195 of bromide.

These results agree with the theoretical numbers, as may be seen by the following table :—

		Theory.		Experiment.
Carbon	8 equiv. . .	48	9·79	9.63
Hydrogen	2 ,, . .	2	·40	·60
Bromine	2 ,, . .	160	44·08	43·71
Silver	2 ,, . .	216	32·65	32·64
Oxygen	8 ,, . .	64	13·08	——
		490	100·00	

On boiling a quantity of bibromosuccinate of silver with water, it gradually decomposes, with evolution of carbonic acid and formation of bromide of silver; the ebullition must be continued until no more carbonic gas is evolved. The resulting mixture is then thrown on a filter; the less soluble portion, which consists chiefly of bromide of silver, is well washed with water; and to the filtrate

which contains a small quantity of silver in solution, a few drops of hydrochloric acid are added. The liquid is then separated from the chloride of silver by means of a filter, and evaporated on a water bath, until of a syrupy consistence. After remaining at rest for four and twenty hours under a bell-jar over sulphuric acid, it is found to contain a considerable quantity of large crystals, which are then separated from the residual syrupy acid by washing rapidly with cold alcohol; the product thus obtained is *tartaric acid.*

A portion of this acid was dissolved in water and divided into two equal quantities. One of these was neutralized with carbonate of potassium, and then the other added to it, which caused the well-known precipitate of the acid tartrate of potassium to form, whereof we made the following carbon, hydrogen, and potassium determinations:—

I. ·202 grm. of substance, gave
·18875 grm. of carbonic acid and
·0540 of water.

II. ·205 grm. of substance, gave
·19200 grm. of carbonic acid and
·0500 of water.

III. ·1545 grm. of substance, gave
·0590 of chloride of potassium.

Percentage composition:—

	I.	II.	III.
Carbon . .	25·49	25·5	—
Hydrogen .	2·9	2·7	—
Potassium .	—	—	20·0

These numbers agree very closely with the theoretical, as may be seen by the subjoined table:—

	Theory.		Experiment.
Carbon 8 equiv. . .	48	25·60	25·49
Hydrogen 5 „ . .	5	2·65	2·80
Potassium 1 „ . .	39·2	20·00	20·0
Oxygen 12 „ . .	96	51·75	——
	188·2	100·00	

This interesting formation of tartaric acid may be thus explained:

$$\underbrace{\left.\begin{matrix}(C_8H_2Br_2O_4)'' \\ Ag\end{matrix}\right\} O_4}_{\text{Bibromosuccinate of Silver.}} + 2\,H_2O_2 = \underbrace{\left.\begin{matrix}(C_8H_2O_4)'''' \\ H_4\end{matrix}\right\} O_8}_{\text{Tartaric Acid.}} + 2\,Ag\,Br;$$

evidently showing that it is derived from four molecules of water.

We have alluded to a syrupy acid which is formed at the same time as tartaric acid, and from which it had to be separated by means of cold alcohol. This we have not investigated, as its nature shows that it would be very difficult to obtain pure, and consequently would require considerable quantities, which, coupled with the expense and labour of obtaining only a few grammes of bibromosuccinic acid, has induced us to lay this part of the investigation aside for the present. It seems, however, probable that it is *pyruvic acid*, which, it will be remembered, is formed from tartaric acid by the loss of carbonic acid and water; and may it not be possible that part of the tartaric acid, at the moment of formation, splits up into carbonic acid, water, and pyruvic acid?

We are now investigating monobromosuccinic acid, from which we expect to obtain some interesting results.

XI.—*On the Composition of the Platinidcyanides.*

By Edward A. Hadow, Esq.

As the platinidcyanides are derived from the platinocyanides, it will be well briefly to mention, in the first place, the mode of formation and properties of the latter. The platinocyanides are a remarkable set of salts belonging to the stable class of double cyanides, exceeding the ferrocyanides in the force with which they retain the electro-negative metal and disguise it to ordinary tests. Concentrated and boiling nitric or hydrochloric acids, alone or mixed, extract no platinum from them; they are unaffected by digestion with peroxide of mercury, and concentrated boiling sulphuric acid liberates cyanide of platinum with difficulty only. They have

the general formula MCy.PtCy or $MPtCy_2$, the platinum in them existing in the state corresponding to protochloride of platinum, so that, before preparing these salts from a solution of bichloride of platinum, it must be reduced to the condition of protochloride, either by sulphurous acid, or by evaporation to dryness and expulsion of half the chlorine by heat. The product in either case is treated with excess of cyanide of potassium until a clear solution is obtained, which, if previously warm and sufficiently concentrated, will deposit on cooling, long prisms of the potassium-salt, from which the other platinocyanides may easily be derived, by precipitating its solution with that of a salt of copper, washing the precipitate, suspending it in water, and decomposing it by a current of sulphuretted hydrogen; the solution which contains hydroplatinocyanic acid, and, after filtration from the sulphide of copper, may be saturated with any required base. A more convenient way I find, in many cases, is to treat the protochloride of platinum directly with the required base, and sufficient hydrocyanic acid to form the double cyanide; the combination takes place easily if assisted by a gentle heat, and it is only necessary to crystallise a few times to get rid of the chloride present in the solution.

These salts are remarkable for the great beauty and variety of the colours their crystals exhibit, while their solutions are transparent and colourless. The platinocyanide of magnesium is, perhaps, the most beautiful of these salts; it forms by slow evaporation large and regular prisms of a deep red by transmitted light, but viewed by reflected light the sides of the prisms exhibit a brilliant beetle-green, and the extremities a deep blue or purple colour. The red salt gently warmed, even under water, becomes bright yellow, which is also the colour of crystals deposited from a solution at a temperature of 160 °F.; heated to 212° F. the salt becomes quite white, and again at a higher temperature bright yellow. These changes of colour correspond to successive losses of water, the ordinary red salt containing 7 equiv.; the yellow, according to Weselsky, 6 equiv. At 212° F. the salt still retains 2 equiv., which are only expelled by a heat of between 300° and 400°, when it becomes anhydrous and again yellow. If a portion of this yellow anhydrous salt be laid on the red salt in powder, it will soon abstract water (from the latter), and a white layer will be formed between two yellow borders, one of these yellow compounds being anhydrous, and the other containing 6 equiv. of water. In-

endeavouring to prepare this salt, I, on one occasion, made use of a method given by Quadrat, which consists in evaporating to dryness mixed solutions of sulphate of magnesia and platinocyanide of potassium, and digesting the dried mass in a mixture of alcohol and ether; instead of which, however, I used only alcohol, and that somewhat weak, and by so doing obtained a solution, which gave, in addition to the ordinary dark red salt, another set of crystals of a paler red, and exhibiting a steel-blue lustre by reflected light, instead of the usual emerald-green of the ordinary salt. Analysis proved it to be a double platinocyanide of magnesium and potassium, having the formula

$$MgPtCy_2 \,.\, KPtCy_2 + 2HO + 5aq = 416{\cdot}5.$$

		Calculated.	Found.	
2Pt	=	47·54	47·2 – 47·1	
4Cy	=	24·97	—	
Mg	=	3·00	3·02	
K	=	9·36	9·41	
2HO	=	4·32	4·40	expelled above 212° F.
5HO	=	10·81	10·97	expelled at 212.
		100·00		

In this, as in many other platinocyanides, a portion of water is retained at 212°. This salt cannot be recrystallised except from a considerable excess of platinocyanide of magnesium, and even when this is present, sudden cooling, or agitation of the saturated solution, causes the separation of the potassium salt free from magnesium.

These platinocyanides, represented by the general formula $MPtCy_2$, may be transformed into the salts termed platinidcyanides, by the action of chlorine, bromine, nitric acid, &c.—a set of compounds characterised in the crystalline form by a peculiar coppery lustre, and to which the general formula $M_2Pt_2Cy_5$ has hitherto been assigned. They are thus represented as differing from the platinocyanides by the addition of an atom of cyanogen to every two atoms of the latter salts.

$$Mg_2Pt_2Cy_5 = 2(MgPtCy_2) \,.\, Cy.$$

This somewhat improbable formula seemed yet to be strongly confirmed by the following facts. Gerhardt at first doubted it,

but afterwards confirmed it by an analysis of the potassium-salt. A determination of the platinum and potassium made by myself agreed so closely with the requirements of the formula as also strongly to confirm it. These salts act like the ferridcyanides in presence of a free alkali,—exerting a powerful bleaching action on cochineal; they also liberate iodine from iodide of potassium, confirming the analogy between the two sets of salts. They evolve cyanogen when heated sufficiently, leaving a residue of platinocyanide. They are produced equally by the action of bromine, nitric acid, and other oxidizing agents on the platinocyanides, showing that no single one of these is essentially necessary for their formation.

But then, on the other hand, the following difficulties presented themselves. The platinum and basic metal remain in the same proportion to each other in the platinidcyanides as in the platinocyanides from which they are derived, the difference being merely an excess of cyanogen in the latter over that in the former. Whence is this cyanogen derived? In the case of the ferridcyanides, the proportion between the iron and the basic metal in the ferrocyanide has been altered by the chlorine, which abstracts a portion of the basic metal, leaving the cyanogen behind to explain the excess found in the ferridcyanide:

$$2(M_2FeCy_3) + Cl = M_3Fe_2Cy_6 + MCl.$$

But to account for that in the platinidcyanides, it is necessary to assume the simultaneous removal, by the action of chlorine on the platinocyanides, of equal proportions of platinum and basic metal:

$$3(MPtCy_2) + Cl = M_2Pt_2Cy_5 + MCl + PtCy;$$

an explanation which appears very improbable to any one who has observed the great stability of the platinocyanides, and the remarkable ease with which the transformation by chlorine occurs. These salts, it is true, have an oxidizing effect in presence of potash, in consequence of which, by the addition of an oxidizable body, they are reduced to platinocyanides; but then it ought to occur with simultaneous formation of free cyanide of potassium:

$$M_2Pt_2Cy_5 + KO + X = 2(MPtCy_2) + KCy + XO,$$

but no free cyanide can be detected as a product of such a reaction in any case. Moreover, there exists another salt, the

ultimate product of the action of chlorine on the platinidcyanide of potassium (the salt chiefly examined), usually represented by the formula $PtCy_2.KCl$, the formation of which from the platinidcyanide is equally difficult of explanation with that of the latter from the platinocyanide; and further still is it difficult to represent the mode of the reduction of the chlorinated salt to the state of platinidcyanide, which, however, actually occurs very readily under the action of reducing agents.

The determination of the proportions between the cyanogen and the platinum at once served to clear up most of these difficulties. The proportion was found to be identically the same in the platinidcyanides as in the platinocyanides; and the difference between the two sets of salts in composition was found to consist in the addition of a certain amount of the chlorine, bromine, or other elementary or compound salt-radical used for their formation,—so that there exist, not one set, but many sets of platinidcyanides, requiring the prefix of *chloro*, *bromo*, &c., to distinguish them. Such being the case, it appeared most probable that Knop's and Gerhardt's salts had been true cyano-platinocyanides, as the above formula indicates, formed under some peculiar conditions, perhaps in presence of excess of cyanide of potassium, so that cyanogen, instead of chlorine, had really been superadded to the original platinocyanide, and that the salt under examination differed from theirs only in containing chlorine in place of cyanogen. I was therefore not a little surprised to find, instead of 1 atom of chlorine to 2 atoms of platinum, which a chlorine-compound analogous to this cyanogen-compound should contain, not above a third of that quantity; accordingly, even if the chlorine ever were truly replaced by cyanogen—which, after several attempts, I failed to effect—the formula $M_2Pt_2Cy_5$ never could represent the composition of the cyano-platinocyanides, the superadded cyanogen being too large in amount by two-thirds.

Considerable difficulty was found in determining the amount of chlorine in the salts, on account of their high atomic weight. Repeated combustions of the chloro-platinocyanide of potassium with nitrate of potash and carbonate of soda gave a proportion of 1 equiv. of chlorine to between 6 and 7 equiv. of platinum. This analytical method proving unsatisfactory, from not giving a probable formula, a synthetical method was tried, with better success; it was found that a solution of platinocyanide acidulated with hydrochloric acid, rapidly and perfectly

decolorises a solution of permanganate of potash, until the platinocyanide has taken up the maximum amount of chlorine, and become converted into the salt, $PtCy_2KCl$, which has been before mentioned as the ultimate product of the action of chlorine on the chloro-platinocyanides, and which might be termed the perchloro-platinocyanide of potassium. As no method could be devised to indicate when the first stage of the change, namely, from platinocyanide into chloro-platinocyanide, is complete, it was not possible to determine the amount of chlorine necessary for its formation in this direct way; but, starting from the chloro-platinocyanide, it was easy to determine by means of permanganate of potash how much *additional* chlorine was necessary to convert it into the perchloro-platinocyanide, the true composition of which had been determined and found to have been correctly represented in its elementary proportions by the formula hitherto given. It was thus found that while 6 equiv. of the platinocyanide, containing 6 equiv. of platinum, required 6 of chlorine for the formation of the perchloro-platinocyanide, a quantity of the chloro-platinocyanide, containing the same amount of platinum, required only 5 equiv. of chlorine to convert it into the same salt, proving that 1 equiv. already existed in this quantity of the salt, and, therefore, that its true composition in the anhydrous state is $6(KPtCy_2)\cdot Cl$. This composition explains its oxidizing power in alkaline solutions, and why no free cyanide can be detected when its force has been spent on an oxidisable body:

$$6(KPtCy_2)Cl + KO + X = 6(KPtCy_2) + KCl + XO,$$

an alkaline chloride, and not a cyanide, being formed. The evolution of cyanogen, and its reduction to platinocyanide when heated, is due to the chlorine partly entering the salt, and displacing cyanogen; (a certain amount of chloride of ammonium is however likewise formed at the time when moisture is present):

$$6(KPtCy_2)Cl = 5(KPtCy_2) + KCl + PtCy + Cy.$$

The salt after this gives a somewhat turbid solution, from PtCy which has been set free. The formation of the salt from the platinocyanide, and its ready conversion into the perchloro-platinocyanide, and the reduction of the latter into the chloro-platinocyanide and platinocyanide successively, by reducing

agents, is due to the successive additions of chlorine in one case, and successive abstractions of it in the other, without any formation or separation of cyanide of platinum, or of chloride of potassium, in either case—

$$6(KPtCy_2) + Cl = K_6Pt_6Cy_{12}Cl$$
$$K_6Pt_6Cy_{12}Cl + 5Cl = 6(KPtCy_2Cl).$$

The chloro-platinocyanide of potassium, as ordinarily dried in a hot-water oven, loses the percentage of water given by Gerhardt in his analysis, but still retains 3 equiv., which, together with the chlorine overlooked, correspond pretty nearly in weight with the excess of cyanogen supposed to exist in the salt, and which thus appears to have been determined by difference only. The composition of the crystallised salt is:

$$Pt_6K_6Cy_{12}.Cl + 3HO + 18aq = 1364{\cdot}5.$$

The direct determinations of chlorine, as before stated, were unsatisfactory, inasmuch as they showed on the average a deficiency of about 0·20 per cent. The salt has a slight tendency to lose water of crystallisation in dry weather. The water was therefore determined in two samples, one dried spontaneously in the air, the other by strong pressure in bibulous paper immediately after removal from its solution, as the two extremes to furnish a correct mean.

	Air-dried.		Dried by Pressure.	Average.	Calculated for 18HO.
18HO Loss per cent at 212° =	11·34	10·9	12·34	11·53	11·87
3HO ,, 400° =	1·94	1·97	—	1·96	1·98

Composition of salt dried at 212°:—

	Found.		Average.	Calculated.
6Pt = 49·27	50·07	48·7	49·34	49·39
6K = 19·68	—	19·92	19·80	19·47
12Cy = 25·83	—	—	25·83	25·95
Cl = 2·76	2·82	2·79	2·79	2·95
3HO = 2·19	2·23	—	2·21	2·24
			99·97	100·00

The quantities of the salt taken for the various determinations varied from 7 to 13 grs. The platinum and potassium were

obtained by evaporation with pure concentrated sulphuric acid, followed by gentle ignition. The cyanogen was determined by combustion of 10·6 grs. with soda-lime.

The above formula represents the empirical composition of the chloro-platinocyanide of potassium. Its true rational composition was discovered on precipitating its solution with a solution of zinc, when it was found to have resolved itself into a platinocyanide, which was precipitated in combination with zinc, and a perchloro-platinocyanide, which remained in solution; and, accordingly, on mixing a solution of the perchloro-platinocyanide, a salt which forms large colourless crystals, with another of the nearly colourless platinocyanide, the mixture, if sufficiently concentrated, will deposit immediately an abundant crop of copper-coloured crystals of chloro-platinocyanide:

$$5(KPtCy_2) + KPtCy_2Cl = K_6Pt_6Cy_{12}Cl.$$

It appears, in fact, to be a double salt of the two.

The solution, accordingly, of the so-called platinidcyanides exhibits the reactions of a mixture of its component salts, and it is thus impossible by any direct tests to ascertain whether either is in excess or not; this point can only be determined by careful crystallisation. By this latter method the formula of the chloro-platinocyanides was further confirmed; the two component salts were mixed in various proportions, and the compound salt was crystallised out, when one or other of its components would be found in excess, unless the right proportions had been taken. The results obtained in this way were not absolutely satisfactory, in consequence of partial decomposition during repeated crystallisation; but they served to counterbalance the determinations of chlorine by analysis, the errors in the numbers obtained being in the opposite direction, and indicating the proportion of 1 equiv. of chlorine to between 5 and 6 equiv. of platinum. It was found that, from whatever solution the chloro-platinocyanide was crystallised, it always contained the same amount of chlorine, so that there appears to be no double salt intermediate between the chloro-platinocyanide and perchloro-platinocyanide; and, accordingly, if a purely cyanogen-platinocyanide existed, it may be concluded from analogy that it would have the composition,

$$5(PtKCy_2) + PtKCy_3 \text{ and not } (PtKCy_2 + PtKCy_3)$$

which the hitherto accepted formula requires. The bromo- and

nitro-platinideyanides so closely resemble the corresponding chlorinated salts as hitherto to have been confounded with them under the general term of platinidcyanides, and as their appearance and facility of formation are so much alike, there is every reason to conclude that they have an analogous composition, being, in fact, double salts of a platinocyanide, and a corresponding perbromo- and pernitro-platinidcyanide, which, like the highest chlorine compounds, are colourless. In the case of nitric acid, NO_6 must represent the chlorine and bromine of the corresponding salts. There appear to be no analogous iodine compounds, since any one of these salts treated with iodide of potassium immediately liberates iodine. But there are analogous compounds containing the salt radical SO_4 in place of chlorine, bromine, &c., and, doubtless, similar compounds with the salt-radicals of other acids: the existence of the sulphuric compound was inferred in the first instance from finding that a solution of a platinocyanide acidulated with sulphuric acid rapidly decolorises a permanganate. The crystallised oxysulpho-platinocyanide of potassium is readily obtained by adding a little peroxide of lead to a saturated solution of platinocyanide of potassium acidulated with sulphuric acid:—each particle of peroxide dropped in becomes instantly enveloped in a moss-like growing mass of the copper-coloured salt.

From a few experiments recently made, it would appear that these remarkable compounds may also be regarded as salts in which the platinocyanide $MPtCy_2$ plays the part of a metal, since, in the sulphuric compound, the sulphuric acid readily admits of replacement by another acid by double decomposition with a baryta-salt: and, accordingly, it seems to be not unlikely that there are oxygen-compounds capable of acting the part of bases, and combining directly with acids to form the per-compounds which by combination with the platinocyanides, form the platinidcyanides. It is on account of the feeble affinity that exists between the platinocyanide (as a compound metal) and the salt-radical, that reducing agents so readily decompose them into the platinocyanide and the corresponding acid, just as they would the corresponding salts of gold, the gold being supposed to represent the platinocyanide in its feebly electro-positive character. If sulphuretted hydrogen be passed into their solutions, which are neutral, they immediately become strongly acid.

The most distinctive reactions between the platinocyanides and perchloro-platinocyanides, are that the former give an abundant *smalt-blue* precipitate with nitrate of suboxide of mercury, and a *flocculent* blue precipitate with salts of copper. The latter give a *white* with nitrate of suboxide of mercury, and a fine *sandy* blue with salts of copper; they liberate iodine from iodides; and if dropped in the solid form into a concentrated solution of platinocyanide of potassium, they are immediately coated with copper-coloured needles.

The platinidcyanides in solution exhibit both sets of reactions, and accordingly, cannot be distinguished until crystallised out, when their dark coppery lustre at once characterizes them. The neatest way of forming the chlorine and bromine salts at once in a state of purity is, to take a concentrated solution of a platinocyanide, measure off a sixth-part and convert it by an excess of chlorine or bromine into the perchloro- or perbromo-platinocyanide, expelling the excess of the chlorine and bromine subsequently by a gentle heat, and then adding the remaining five-sixths of platinocyanide; in a very short time the double salt will form abundantly in a state of perfect purity.

XII.—*On the Stibethyls and Stibmethyls.*

By G. B. Buckton, Esq., F.R.S.

Chemists are already aware, through the researches of Dr. Hofmann, that zinc-ethyl reacts on terchloride of antimony in a manner similar to that shown by terchloride of phosphorus;—in the former case, triethylstibine is formed, in the latter case, triethylphosphine. The same successful labourer in this field of chemical inquiry, in his profound and complete history of ammonia, lately communicated to the Chemical Society, groups these bodies as primary triamines, or ammonias in which antimony and phosphorus severally play the parts of nitrogen, and three equivalents of ethyl those of hydrogen.

The following experiments were undertaken with the intention of testing how far the compounds of antimony with methyl and ethyl, were limited to the ammonia-type, and more particularly to determine whether, by assimilating more than three molecules of methyl, &c., bodies might arise referable to the types of antimonious and antimonic acids.

Triethylstibine is known to combine with two equivalents of chlorine or iodine to form its haloïd salts. If substitution could be effected, through zinc-ethyl, in these substances, a pentethylated radical would arise, showing the antimony in a complete condition of saturation.

Coarsely powdered antimony attacks iodide of ethyl readily, when sealed in tubes, and exposed to a temperature of about 140° C. An oily liquid is formed, composed of biniodide of triethylstibine, with probably a little teriodide of antimony. This biniodide, $Sb(C_4H_5)_3I_2$, produces considerable heat when mixed with zinc-ethyl, a pasty mass being formed, upon the surface of which a yellowish liquid floats. Distillation is attended by an abundant evolution of inflammable gas, which is charged with the vapour of triethylstibine. To remove as far as possible the inconvenience of these dense white antimonial fumes, the first distillation is best performed in a quilled receiver, the tube of which is plunged into water.

The yellowish heavy liquid, obtained as above, was rectified in an atmosphere of coal gas.

The first portion contained a little ether, which was separated, after which the temperature rose to 150°, between which and 170° C. all the liquid products passed over.

The fraction boiling below 160° C. had the properties of triethylstibine, but gave numbers slightly higher than those required by theory.

	Theory.		Experiment.	
Sb	129	59·73	—	—
C_{12}	72	33·33	33·51	33·97
H_{15}	15	6·94	7·17	7·39
	216	100·00		

Triethylstibine, when pure, is a colourless and limpid fluid, having a faint odour, which can scarcely be styled alliaceous. An unpleasant and very persistent taste is left in the mouth when a small portion only of its vapour has been inhaled. It is spontaneously inflammable in air, but may be kept unchanged under a layer of water. It mixes with bromine, under water, without disengaging any noticeable quantity of gas, and the oily bibromide of triethylstibine is formed. With hydrochloric acid hydrogen gas is liberated, and the corresponding non-fuming bichloride is produced.

Triethylstibine is a very stable body, and distils without

change. Here it differs from Stanethyl, which, as Dr. Frankland has shown, deposits when heated, half its quantity of tin, and passes into stannic diethyl.

Lowig and Schweitzer found the boiling point of triethylstibine to be 159° C.

A combustion of the samples boiling between 160° and 170° C., showed a considerable increase in the percentage of both carbon and hydrogen.

Although the numbers obtained, approach more nearly the composition of tetrethylstibine than that of pentethylstibine, it is thought more probable that the latter substance is really contained in the mixture. The percentage of carbon and hydrogen was not increased by another rectification of the sample, and it soon became evident that the body was broken up by heat. This observation furnishes an explanation of the copious liberation of gas noticed during the distillation of biniodide of triethylstibine with zinc-ethyl.

	Tetrethylstibine.		Sample 1.		Sample 2.	
Sb	129	52·65	—	—	—	—
C_{16}	96	39·19	37·51	37·44	35·96	35·44
H_{20}	20	8·16	7·90	8·01	7·43	7·39
	245	100·00				

The decomposition of such a body by heat is analogous to that of pentachloride of antimony, which is thus known to yield chlorine gas and the terchloride. In the same manner,

$$Sb(C_4H_5)_5 = Sb(C_4H_5)_3 + C_4H_4 + C_4H_5H.$$

The existence of a stibium compound, containing more than three molecules of ethyl, was confirmed by the deportment of the sample under examination towards bromine. A portion of the fuming liquid was thrown up into the head of an eudiometer tube standing over mercury, and small quantities of bromine were introduced from time to time. The mixture was attended with a violent action, and a bulk of permanent gas was formed. As the neutral point was approached, all visible action ceased, but when the bromine was in slight excess, a partial absorption of gas was noticed.

As triethylstibine unites with bromine to form the bibromide without liberation of gas, the appearance of ethylene and hydride of ethyl can only be explained by the presence of a more complex ethylated radical than triethylstibine.

The absorption of gas also would thus be easily explained.

$$Sb(C_4H_5)_5 + 4Br = Sb(C_4H_5)_3Br_2 + C_4H_4Br_2 + C_4H_5H.$$

Triethylstibine passes into the non-fuming bichloride also more readily with concentrated hydrochloric acid than the substance here described, which loses its character of spontaneous inflammability only after long boiling.

It is remarkable that zinc-ethyl is not attacked by bichloride of triethylstibine, even when the mixture is raised to its boiling point.

The most characteristic salt of triethylstibine is the bisulphide, which is easily formed by heating the radical with alcohol and sulphur. It crystallises in long silky needles, which are readily soluble in water. This salt is rapidly decomposed by boiling in excess of aqueous cyanide of potassium. The cyanide is in this manner converted into sulphocyanide of potassium, and triethylstibine is liberated in white fumes.

If the mixture containing the higher stibium-radical be boiled with alcohol and sulphur, there is formed, together with bisulphide of triethylstibine, a considerable quantity of bisulphide of ethyl. This substance becomes immediately evident by its powerful and repulsive odour.

Although triethylstibine is remarkably persistent in itself, its salts are in general easily reduced.

The most convenient method of obtaining the radical triethylstibine is by distilling its salts with granulated zinc. As the biniodide is easily formed, it is well suited for such an operation. The action is set up with some energy, and the products are most conveniently received under water.

I have failed in forming substitution-products by bringing together triethylstibine and bisulphide of carbon. The same failure also has happened in my attempts to cause a reaction between triethylstibine and bibromide of ethylene. An interesting body from triethylphosphine, homologous to sulphocarbamate of ammonium, has been obtained by Hofmann:

$$2\,PE_3 + C_2S_4 = \left.\begin{matrix}(C_2S_2)'' & E_2P \\ & E_4P\end{matrix}\right\} S_2.$$

With triethylstibine the tubes invariably burst at a temperature of 140° C., and below this point no change appeared in the materials.

Having some quantity of triethylstibine at my disposal, a few experiments in confirmation of those of M. Löwig were made.

On the Salts of Tetrethylstibine.

Triethylstibine was mixed with a slight excess of iodide of ethyl. In the course of a few hours, a mass of fine crystals of iodide of tetrethylstibine was obtained.

Iodide of tetrethylstibine, when mixed with zinc-ethyl and distilled, yields the same results as if biniodide of triethylstibine had been employed. Iodide of zinc, fixed gases, and a mixture of two radicals incapable of separation by heat were obtained.

Oxide of Tetrethylstibine is very soluble in water, and is uncrystallizable. When heated above 100° C. it undergoes decomposition, with liberation of white fumes of triethylstibine.

Sulphate and nitrate of tetrethylstibine are crystalline salts.

Chloride of Tetrethylstibine is also crystalline. When dissolved in water, and mixed with bichloride of platinum, it yielded a fine yellow crystalline salt, which was but little soluble in alcohol.

When ignited and separated from the antimony, the following analytical result was obtained.

0·7856 grm. of salt, gave 0·1752 grm. of platinum, which accords most nearly to the formula,

$$Sb(C_4H_5)_4Cl.PtCl_2$$

	Theory requires.		Found.
Sb . .	129·0	28·63	—
C_{16} . .	96·0	21·30	—
H_{20} . .	20·0	4·44	—
Cl_3 . .	106·5	23·65	—
Pt . .	99·0	21·98	22·31
	450·5	100·00	

Löwig obtained a salt much richer in platinum, to which he assigns the composition,

$$3PtCl_2, 2(Sb(C_4H_5)_4Cl).$$

Action of Zinc-methyl on Biniodide of Trimethystibine.

As the methyl-molecule is simpler in structure than that of ethyl, it was thought that a penta-methylated body might possibly resist decomposition during distillation. The biniodide of trimethylstibine may be obtained in beautiful crystals, by acting on

metallic antimony with iodide of methyl, at a temperature of 140° C. As these crystals were found to decompose zinc-methyl energetically, an appeal was again made to experiment.

The materials were mixed slowly in a retort, and after the first action had subsided, the mass was submitted to a temperature of 100° in a water-bath, which removed the excess of zinc-methyl and ether. Subsequently, the distillation of the solid mass was completed over the sand bath.

In this way, a heavy pale-coloured liquid was obtained, which, after agitation with water and weak acid, was rectified in an atmosphere of coal gas, heat being applied by a water-bath.

Fractions were taken between 80°—86°, 86°—96°, 96°—100° C.

All these samples had the following properties:

They were oily bodies with faint odours, heavier than water, with which they did not mix. When exposed to the air, they were not spontaneously inflammable, neither did they, at ordinary temperatures, give off white fumes. When dropped on a warm surface, however, they ignited and burnt with a luminous flame, accompanied by a dense antimonial cloud.

The following numbers were obtained by analysis of these samples:—

	80°—86°		86°—96°	96°—100°	
Carbon . .	21·99	21·20	26·90	30·18	31·64
Hydrogen .	5·08	5·23	5·92	6·83	6·98

For comparison, the numbers required by theory for antimony with three, four, and five equivalents of methyl, are appended.

Sb Me$_3$		Sb Me$_4$		Sb Me$_5$	
Sb	74·25	Sb	68·37	Sb	63·19
C_6	20·69	C_8	25·39	C_{10}	29·46
H_9	5·16	H_{12}	6·34	H_{15}	7·35
	100·00		100·00		100·00

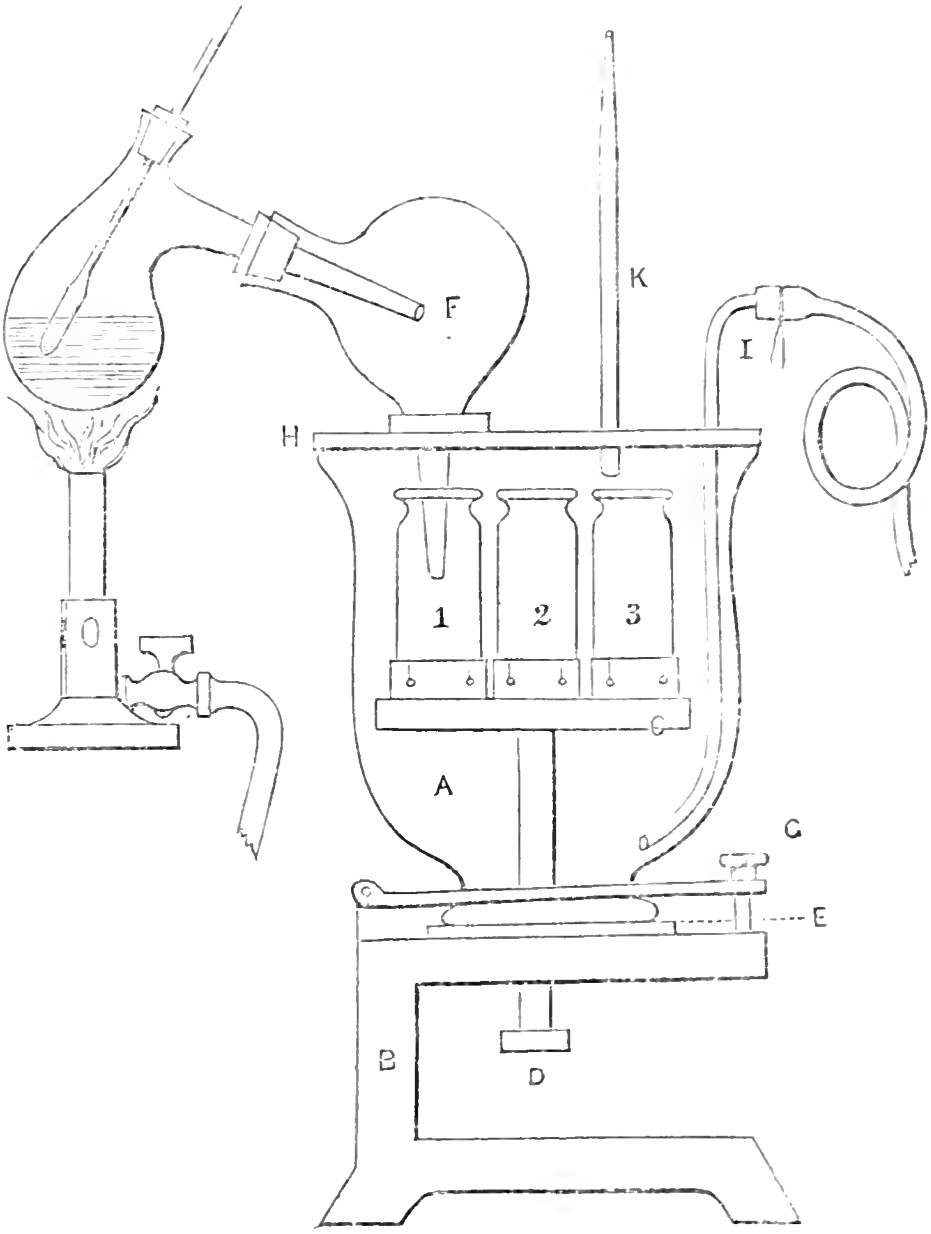
Notwithstanding the circumstance that the above samples are not spontaneously inflammable (a character pre-eminently shewn by trimethylstibine), the composition of No. 1, seems to indicate its identity with that body. Before being confident with reference to the composition of Nos. 2 and 3, some weight must be given to an observation here made, viz., that in the decomposition of zinc-methyl by a high temperature, instead of gases being eliminated, as is known to be the case with zinc-ethyl, hydro-carbons are pro-

duced which burn with a smoky flame. These substances I have not yet been able to examine, but it would appear that the methyl-molecules undergo duplication, and thus give rise to bodies possessing high boiling points.

It is therefore possible, that pentamethylstibine may be resolved by heat into trimethylstibine and such a hydrocarbon. This would account also for the excess in the carbon and hydrogen given by analysis of sample No. 3.

In conclusion, it is thought that a reviewal of these experiments, in both the ethyl and methyl series, will justify the conclusion that the higher stibium organo-radicals exist. A better method for their isolation however, is still a desideratum.

Apparatus for general fractional Distillation in Carbonic Acid Gas.



A. Inverted bell glass with open neck.

B. Stand with thick vulcanized indian rubber collar E.

C. Circular table with sockets for holding bottles 1, 2, 3, &c.

D. Thick glass rod, sliding air-tight through collar and stand, by which the table and bottles may be raised, lowered, or rotated at pleasure.

F. Quilled receiver and retort.

I. and K. Tubes for entrance and exit of carbonic acid or other gas.

G. Clamp with forked arm, to secure the bell to the stand, and permit the table to rotate eccentrically, if required. The tube of the receiver may thus be introduced into any one of the bottles.

H. Slate cover, which may be ground to fit the lip of the bell, or simply luted to it with linseed.

XIII.—*On Crystallized Sodium and Potassium.*

By Charles Edward Long.

In endeavouring to prepare perfectly bright specimens of sodium and potassium, I have succeeded in obtaining large crystals of both metals. I will briefly describe the method now employed.

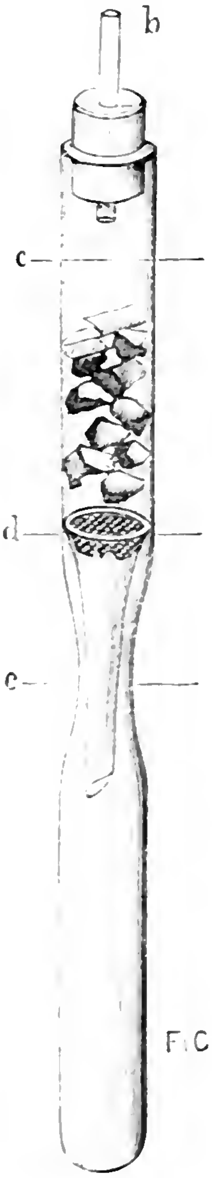


FIG. 1

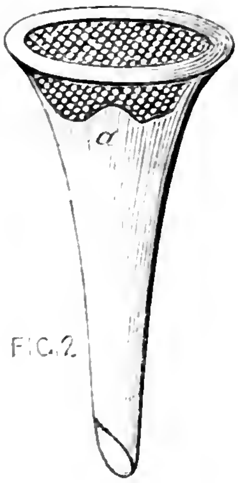


FIG. 2

A piece of the best combustion tube about $2\frac{1}{2}$ feet in length, and $\frac{3}{4}$-inch in bore, is sealed up at one end, and contracted before the blowpipe at about one-third of its length from the sealed end (fig. 1). A glass funnel with a wide rim (fig. 2) is then prepared so as to fit into the tube as represented, care being taken that the funnel fits *at the rim alone.* Into the filter is introduced a piece of wire gauze, in which a small hole has been cut at *a* (fig 2). The sodium (or potassium) is now introduced into the upper part of the tube in fragments which have been freed from all adhering oxide, and especially from rock-oil, by cutting the metal clean with a knife. Before introducing the metal, the tube is filled with coal-gas which has been dried and partly purified by passing through oil of vitriol. For this purpose, the delivery tube is passed through the tube *b,* which is fitted with a cork into the larger tube.

After the introduction of the metal, the gas is still passed into the tube; the delivery tube is then drawn out and the tube *b* is lightly corked. The large tube is now drawn out and sealed before the blowpipe at *c,* care being taken to avoid melting the metal, lest it should attack the glass and render it brittle. The metal is next fused in the upper part of the tube, and partially

poured off from the oxide, so as to present a bright surface for the absorption of any oxygen there may be in the tube. The whole is then allowed to stand for several days, after which the metal is again melted, poured through the filter into the lower portion of the tube, and allowed to solidify. The tube is now cautiously heated at *d*, so as to detach the rim of the filter, which will then readily fall back to the top of the tube on reversing its position, leaving a perfectly clean surface of tube of about 3 inches. The lower tube may now be drawn out and sealed at *e*.

In this manner either metal may be obtained without the slightest tarnish or oxidation. In order to crystallise the metal, it is fused over a Bunsen's lamp, and allowed to cool; as soon as the solid points of crystals appear on the surface, the liquid portion is poured off by suddenly inclining the tube. Specimens prepared in this manner 18 months ago, still retain their lustre unimpaired.

Sodium.—Sodium presenting a perfectly clean metallic surface, is not silver-white, but is of a most beautiful rose colour. The colour is best seen when a ray of light falling upon a surface of the metal is reflected back from a second surface of sodium, and again reflected from the first, so that more of the light of the primitive ray is decomposed than by direct reflection, since the great number of undecomposed reflected rays entirely masks the small number of pink rays, as is the case with silver, which is really yellow and not white. The pink colour of sodium is brought out more strongly by contrasting the metal with bright potassium, which has a greenish-blue tinge.

Sodium is obtained in large octahedra by crystallisation. It does not crystallise in the regular system, but most probably in the quadratic system. As it is impossible to measure the crystals by reflection, owing partly to their being enclosed in a glass tube, but chiefly to the irregularity of the faces which are always striated in a direction at right angles to the major axis, I was only able to measure the facial angles by using a narrow tube provided with an arc, and across which a fine hair was stretched. Unfortunately I have not obtained any crystals with the base-angles well defined. The following are measurements of the angle of the apex:—

		Angle of apex.		
		1	2	3
Crystal I.	face *a* . .	49°·8	50°·0	50°·5
	face *b* . .	50°·5	50°·0	49°·5
Crystal II.	. . .	49° 5	50°·0	49°·5

Potassium.—Has a greenish or greenish blue tint. The beautiful green colour of the vapour may be observed by volatilizing a small portion of the metal in a sealed tube containing no oxygen. It is much more crystalline metal than sodium, but is more difficult to obtain in good crystals, since it passes almost immediately from the liquid to a pasty state. The crystals present an almost smooth metallic appearance for a few moments after the liquid metal has been poured off. Suddenly they assume the appearance of frosted silver, a network of minute lines darting out in every direction. For this reason, they disperse light much more than sodium crystals, whereby the real colour of the metal is effectually masked.

Potassium crystallises in obtuse octahedra belonging to the quadratic system. The following are the measurements of the three facial angles of one of the crystals. In crystal II, I was only able to measure one of the angles of the base:—

			1	2	3
Crystal I.	Angles of base	α	52°·0	52°·0	52°·0
		β	52°·0	52°·0	52°·0
	Angle of apex	γ	75°·5	75°·8	76°·0

		1	2	3	4
Crystal II.	Angle of base	52°·0	51°·5	51°·8	51°·8

XIV.—*On Zinc-methyl.**

By J. A. Wanklyn, F.R.S.E.,

DEMONSTRATOR OF CHEMISTRY IN THE UNIVERSITY OF EDINBURGH.

Zinc-methyl was discovered rather more than ten years ago by Frankland. It was then obtained nearly pure, but in quantity so small, that many of its leading physical properties, including its vapour-density, specific gravity, and boiling point, were not determined. More recently, the subject has again been taken up by the same chemist, who this time operated upon several pounds of materials, and under conditions widely differing from those of his former experiments.

* An abstract of this paper was read before the Royal Society of Edinburgh, April 2nd, 1860.

The latter investigation has, however, not been so successful as the former, inasmuch as it has given no pure zinc-methyl, having instead disclosed peculiar and unlooked-for difficulties in the preparation of that compound.

When zinc and iodide of methyl are heated together in closed tubes, the following reactions take place:—

$$(1) \quad . \qquad . \quad Zn_2 + C_2H_3I = ZnI.ZnC_2H_3$$
$$(2) \quad . \qquad . \quad Zn_2 + 2C_2H_3I = 2ZnI + C_2H_3.C_2H_3.$$

At moderate temperatures, the former reaction predominates; at higher temperatures, the latter. When only iodide of methyl and zinc are employed, and no ether is used, it is impossible to obtain complete decomposition of the iodide without at the same time obtaining much gas. This circumstance renders it impracticable to prepare much zinc-methyl by this method, as the high pressure of the generated gas necessitates the employment of very small tubes. The copper digester, which Frankland employs for the manufacture of this class of substances cannot be made to replace the small glass tubes. Frankland has found that when the materials are heated in the copper digester, no pure zinc-methyl can be obtained.

A mixture of ether with iodide of methyl is easily converted into iodide of zinc and ethereal solution of zinc-methyl. Here, however, a fresh difficulty arises. Fractional distillation does not avail to separate ether from zinc-methyl. And so pertinaciously do these two liquids cling to one another, that it is even a matter of doubt, whether a chemical compound does not exist between them.

To this point our knowledge was advanced by the publication of Frankland's paper* last year.

My attention was drawn to this subject, in the course of my investigation of the compounds formed by methyl with the alkali-metals. These compounds are prepared by acting upon zinc-methyl with the alkali-metals. At first I employed the solution of zinc-methyl in ether, but I found the ether to be a very troublesome complication, and therefore was led to enquire whether it were really impossible to obtain zinc-methyl in a state of purity and at the same time in considerable quantity.

*Ann. Ch. Pharm. cxi., 62; also Bakerian Lecture, 1859.

During my experiments, I observed the fact that a strong ethereal solution of zinc-methyl, equally with ether, renders the decomposition of iodide of methyl by zinc easy and comparatively unaccompanied by the evolution of free methyl. Thereupon I tried a stronger solution of zinc-methyl and found it also effectual. A still stronger solution was also successful, and it seemed that even pure zinc-methyl itself possessed the same property. Here, then, was an available method of making pure zinc-methyl. Strong ethereal solution of that compound was first prepared. The strong ethereal solution was next mixed with iodide of methyl and sealed up with zinc; then, after digestion in the water-bath, distilled. In this manner, a stronger solution of zinc-methyl was prepared. By repeating the process, a sufficient number of times, the amount of ether originally taken was made to bear a very trifling ratio to the ultimate product; and indeed could be made to vanish altogether.

In evidence of the practicability of the plan just proposed, I may mention, that the product from a single tube, which had undergone four successive digestions, amounted to about half an ounce, and proved to be zinc-methyl as pure as the gramme or two obtained by Frankland ten years ago.

Before giving the analysis of this sample, I will just mention a few particulars connected with its preparation, which may be interesting to any one who may desire to prepare the compound.

The digestions were all made in the water-bath, the substance being always contained in glass tubes. In order that an ounce or two of iodide of methyl might be, with safety, heated in a single tube, the precaution was taken of opening the tube several times in the course of the digestion. By this means, a dangerous accumulation of hydro-carbon gas was avoided. The distillation, of the zinc-methyl was made over the naked flame. Finally, previously to the last distillation, a digestion with metallic-zinc, without any fresh iodide of methyl, was made.

I may also mention that iodide of zinc forms with zinc-methyl, a crystalline compound of great beauty and very different in appearance from the crystalline compound between iodide of zinc and zinc-ethyl. This compound, containing probably one equivalent of zinc-methyl combined with one equivalent of iodide of zinc, I regard as the representative of the so-called iodide of mercury-methyl obtained by Frankland.

Double zinc compound.

$$Zn_2 \begin{cases} C_2H_3 \\ I \end{cases}$$

Double mercury compound.

$$Hg_2 \begin{cases} C_2H_3 \\ I \end{cases}$$

Passing on to the properties of the half-ounce of zinc-methyl, whose preparation I have just described:—It was highly inflammable and acted upon water with explosive violence, agreeing with Frankland's description of that compound. In one particular, however, our observations do not accord with one another. The poisonous nature of the fumes, their action upon the nervous system, which Frankland mentions,* I have not been able to verify. I have distilled zinc-methyl more than a dozen times, and been much exposed to its fumes, and still have not been able to mark any particular effect upon myself.

In addition to the properties detailed by Frankland, I have to record that zinc-methyl in a state of purity, is very permanent. If carefully excluded from the atmosphere, it will bear without decomposition a temperature of at least 200° C.

At about 270° C. it begins to be reduced to metallic zinc and hydro-carbon gases.

I have made an analysis of the sample of zinc-methyl with the following results:—

I. ·1134 grm. of the liquid were passed up into a graduated tube standing in the pneumatic trough and filled with water. Hydride of methyl was evolved, measuring 48·77 cubic-centimeters (dry) at 760 m.m. pressure and 0° C. This equals ·034898 grm. by weight:—

Hydride of methyl per cent. = 30·77.

II. ·1172 grm. similarly treated gave ·0361 grm. of hydride of methyl or 30·83 per cent.

The theoretical percentage of hydride of methyl, which pure zinc-methyl should give on treatment with water equals 33·51.

These results do not depart from the theoretical quantity further than that which Frankland published ten years ago. His percentage of hydride of methyl was 29·91.

In estimating the value of these determinations, it should be borne in mind that the quantity of hydride of methyl obtained represents its equivalent of unoxidized zinc-methyl. The slightest oxidation tells enormously upon the analysis; for not only does

* Ann. Ch. Pharm. lxxi., page 214.

the oxygen lower the percentage of methyl by its presence, but by combining with a certain amount of zinc-methyl, it still further lowers the percentage of methyl which can decompose water.

The great violence of the reaction between zinc-methyl and water is also a source of loss, especially when water and not mercury is the confining fluid, as was the case in both Frankland's analysis and my own.

A determination of the vapour-density by Gay Lussac's method was also made. ·1163 grm. of zinc-methyl were employed. The temperature to which the vapour was exposed was 100° C; the boiling point of the compound lying between 50° C and 60° C. The experiment gave 3·291 as the vapour density of zinc-methyl. If, as seems likely, the condensation of this compound is analogous to that of its ethyl representative, the theoretical vapour-density is 3·299, a number which is nearly identical with that found by experiment.

The accurate determination of its boiling point, and also of the specific gravity in the liquid state, I hope shortly to have an opportunity of making, as I expect at no very distant period to be in possession of several ounces of pure zinc-methyl.

I cannot conclude this paper without calling attention to the very remarkable state of condensation, disclosed by examination of the vapour-densities of zinc-ethyl, zinc-methyl, mercury-ethyl, mercury-methyl, and indeed of all the so-called organo-metallic bodies so far as has yet been investigated.*

It has been said, the metals are the strict representatives of hydrogen: and yet, in not a single compound of a metal with a hydro-carbon radical, has the metal been found in the state of condensation of hydrogen. If we write the formulæ of equal volumes of several of these bodies, we arrive at the following expressions:—

Zinc-methyl. $\left.\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right\} Zn_2$; Zinc-ethyl. $\left.\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right\} Zn_2$; Mercury-methyl $\left.\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right\} Hg_2$; Mercury-ethyl $\left.\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right\} Hg_2$;

Distann-methyl. $\left.\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ C_2H_3 \end{matrix}\right\} Sn_2$; Distann-ethyl. $\left.\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{matrix}\right\} Sn_2$.

Writing also the formulæ of equal volumes of the hydrogen and oxygen terms for comparison with the former:—

Hydride of methyl.	Hydride of ethyl.	Methyl-ether.	Ethyl-ether.
$\left.\begin{matrix}C_2H_2\\H\end{matrix}\right\}$;	$\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}$	$\left.\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\}O_2$	$\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2$.

Inspection of the above shows that, considered as to the state of condensation in their hydro-carbon compounds, the metals do not represent hydrogen: mercury and zinc represent oxygen.

Nor is this peculiarity confined to the organic case. Deville and others have recently taken the vapour-density of various metallic chlorides and have found that these likewise are present in a more condensed form than their hydrogen representative. Whereas the formula of hydrochloric acid is $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$, the formula of an equal volume of metallic chloride is $\left.\begin{matrix}M_2\\Cl_2\end{matrix}\right\}$ or $\left.\begin{matrix}M_4\\Cl_6\end{matrix}\right\}$ &c.

XV.—*On some derivatives from the Olefines.*

BY FREDERICK GUTHRIE.

III.

THE introduction of nitroxine* into organic bodies, and the formation of the so-called nitro-compounds, has been hitherto effected, with apparently a single exception† by the action of nitric acid, either alone or in presence of sulphuric acid. The reason of this is obvious:—such introduction has, in every case, consisted in the *replacement* of hydrogen by nitroxine. The nitric acid offers its fifth atom of oxygen to the hydrogen being replaced, while, the nitroxine replaces it. Such replacement is of course double recomposition expresssed generally by the equation,

$$C_m \ldots H_n + p(ONO_4) = C_m \ldots H_{n-p}(NO_4) + pHO$$

and is quite parallel to the reaction attending the formation of

*It will be found convenient to call NO_4 *nitroxine*, a compact term, recalling the analogy which this molecule bears to chlorine, iodine, etc.: Accordingly the nitrites, $MONO_3$, will be nitroxides MNO_4 as has been sometimes proposed.

Further regarding the nomenclature, as with the chlorides, $C_4H_2Cl_2$ is bichlorethylene, $C_4H_4Cl_2$ bichloride of ethylene, etc.:—So with the nitroxides:

$C_{20}H_7NO_4$, Nitroxinapthaline

$C_{10}H_{10}2NO_4$, Binitroxide of Amylene, etc.

†See below; nitroxinapthaline.

the chlorine substitution derivatives obtained by the action of chlorine,

$$C_m \ldots H_n + p(\mathrm{Cl\ Cl}) = C_m \ldots H_{n-p}\mathrm{Cl} + p\mathrm{HCl}$$

and probably also to that which occurs when chlorine is introduced by means of hypochlorous acid.

The formation of binitroxide of amylene, $C_{10}H_{10}.2NO_4$, by the action of nitric acid upon amylene,* immediately suggested the question:—May the olefines whose privilege it is to combine directly with two atoms of the halogens, without elimination of hydracids, behave in a similar manner towards nitroxine?

If nitroxine, prepared by heating anhydrous nitrate of lead, be passed through an empty bottle and then into a flask containing amylene, the gas is instantly absorbed and the amylene gradually becomes converted into a pasty mass of minute crystals. To avoid loss, the flask containing the amylene should be surrounded by a freezing mixture. The product is thrown upon a filter, washed with cold alcohol in order to remove an oily liquid which accompanies the crystals, then recrystallised from boiling ether, and dried in *vacuo* over sulphuric acid.

I. 0·2682 grm. gave 0·3664 grm. carbonic acid and 0·1572 water.
II. 0·2290 grm. gave 32·3 cc. of nitrogen at 760 mm. and 0° C which gives,

	Calculated	Found I.	Found II.
C_{10} . .	37.09	37·26	,,
H_{10} . .	6·18	6·51	,,
N_2 . .	17·28	,,	17·66
O_8 . .	,,	,,	,,

This substance is therefore the binitroxide of amylene $C_{10}H_{10}.2NO_4$ and is identical with the crystalline body obtained by the action of nitric acid upon amylene (see II). It is curious as being the only known nitroxine-isotype of Dutch liquid, but more remarkable, in this latter manner of its formation, as furnishing the only instance in organic chemistry of the behaviour of free nitroxine as a halogen without the elimination of hydrogen. Bintroxide of amylene is but slightly soluble in cold, but readily in boiling alcohol; it dissolves in ether and in bisulphide of carbon

*See II.

but is perfectly insoluble in water. It crystallises in small square and rectangular, colourless, transparent plates.

Heated by itself in a dry tube, binitroxide of amylene decomposes exactly at 95° C., giving rise to a gas and to a liquid heavier than water. The decomposition of a portion having been effected in a very strong sealed tube by heating to 100° C., the tube on opening gave off much gas, which reddened moist litmus paper. Another portion was treated in the same way in presence of water. After opening the tube, neutralizing the acid water with ammonia, filtering, and evaporating to dryness on a water bath, a residue was obtained, which gave off nitrogen on being heated. Accordingly, the gas evolved from the binitroxide of amylene was nitrous acid, NO_3, or nitroxhydric acid HNO_4.

The next point was to determine the nature of the liquid product, the supplementary factor to binitroxide of amylene, which appears in the preparation of that body.

The filtrate and alcoholic washings from binitroxide of amylene, after evaporation for some hours on a water bath, washing with water and drying, yielded an amber-coloured transparent liquid, heavier than water and immiscible with it.

Neither this liquid nor the binitroxide of amylene underwent any change on being kept for several days in an atmosphere of nitroxine.

On analysing the liquid :

0·2586 grm. gave 0·3882 grm. of carbonic acid and 0·1717 water.

The substance whose composition corresponds most closely with these numbers, is a mixture of equivalent quantities of binitroxide of amylene with nitrate of amyl.

	$C_{10}H_{10}.2NO_4$ $C_{10}H_{11}O.NO_5$	Found.
C . .	40.67	40·94
H . .	7.12	7·37

Although the presence of amyl would point to the disintegration of another molecule of amylene, the above given composition of this mixture is rendered probable on the following grounds :—On heating to 95° C.,* it undergoes decomposition, whereupon the temperature rises spontaneously to 170° C., and the greater

* Identical with that at which $C_{10}H_{10}.2NO_4$ is decomposed

quantity of the liquid passes over. On rectifying, a portion was obtained which boiled almost constantly at 160° C. Of this,

0·2263 grm. gave 0·3850 grm. carbonic acid and 0·1712 grm.

	$C_{10}H_{11}ONO_5$	Found.
C . .	45·11	46·40
H . .	8.27	8.40

On boiling a portion of this distillate with an alcoholic solution of caustic potash, nitrate of potash was formed. The original liquid also gave rise to nitrate of potash under the same circumstances.

Nitrate of amyl also appears among the liquid products formed when binitroxide of amylene is heated by itself.

Heated with quick lime, binitroxide of amylene gives rise to an aromatic body, differing from valeral and probable amylenic ether $C_{10}H_{10}O_2$.

The actions of sulphide of ammonium, nascent hydrogen, and other reducers, upon binitroxide of amylene, will be well worthy of study.

As yet, my attempts to combine nitroxine with ethylene have not been successful.

Neither protoxide nor binoxide of nitrogen has any action upon amylene. The affinity of amylene for nitroxine is so great that by means of this hydrocarbon, a very small trace of nitroxine may be detected in the above named nitrogen-oxides. Thus if amylene be added through a funnel tube to a flask containing copper and nitric acid which is kept quite cold and from which the evolved gas has expelled the air, crystals of binitroxide of amylene are continuously though slowly formed; but if the binoxide of nitrogen be first absorbed by protosulphate of iron and then expelled thence by heat* and made to pass through amylene in an apparatus from which a current of carbonic acid has expelled the air, no change occurs.

Nitroxinapthalin. (Nitronapthalin.)

The laborious reseaches of Laurent† and others have long since established the claim of napthalin to be an olefine. It combines directly with chlorine to form bichloride of napthalin $C_{20}H_8Cl_2$, and although it may unite with four atoms of halogen as in the

* Bunsen's Gasometry. Engl. Ed. p. 51.
† Ann. Ch. Phys., 1835, lix.

quadrichloride $C_{20}H_8Cl_4$, in the terchloro bromide $C_{20}H_8Cl_3Br$, and in their numerous idiotypes,

$C_{20}H_6Cl_2Cl_4$ quadrichloride of bichlornapthalin.
$C_{20}H_6Br_2Cl_4$ quadrichloride of bibronapthalin,
etc. etc.

yet, as we have already seen in examining the behaviour of ethylene and amylene towards chloride of sulphur, and as we shall abundantly see in the sequel, this assumption of four haloid atoms is quite consistent with the nature of the olefines isotypic with ethylene. Like ethylene, napthalin combines with anhydrous as well as with hydrated sulphuric acid, and finally in napthalamine $C_{20}H_8HN$ we find it still preserving the biatomic character of an olefine, taking the place of two atoms of hydrogen.

Laurent's examination of the action of nitric acid on napthaline resulted principally in the discovery of three nitroxine-replacement derivatives, idiotypic not with the bichloride of napthalin, but with napthalin itself.

Nitroxinapthalin . . .	$C_{20}H_7(NO_4)$
Binitroxinapthalin . .	$C_{20}H_6(NO_4)_2$
Trinitroxinapthalin . .	$C_{20}H_5(NO_4)_3$

Bearing in mind, on the one hand, the analogy which these bodies have to the chlorine-idiotypes of ethylene, and on the other, the above described direct union of amylene with nitroxine, we might *à priori* expect to obtain nitroxide of napthalin or binitroxide of napthalin by the action of nitroxine on napthalin. So that, although Laurent gives this reaction as a method of preparing nitroxinapthalin, yet, as no analysis appears to have been made of the body so produced, I thought it worth while to comfirm Laurent's experiment.

If napthalin be thrown into a flask containing an excess of nitroxine, considerable heat is developed, scanty white fumes are formed, which quickly subside, and an oily liquid results which solidifies on cooling. To ensure complete reaction, the flask is corked with an excess of nitroxine, and the product is repeatedly shaken and melted. After re-fusion under water, drying, and recrystallisation from ether, a product was obtained which gave on analysis

0·4202 grm. gave 1·0707 grm. CO_2 and 0·1590 grm. water.

	$C_{20}H_7(NO_4)$	Found.
C . .	69·36	69·49
H . .	4·05	4·20

The substance formed is therefore undoubtedly nitroxinapthalin. We accordingly find that nitroxine, in its behaviour towards napthalin, more closely resembles bromine than chlorine; for while the former gives bromonapthalin, the latter gives bichloride of napthalin,

$$\begin{aligned} C_{20}H_{8} + 2Cl &= C_{20}H_{8}Cl_{2} \\ C_{20}H_{8} + 2Br &= C_{20}H_{7}Br + HBr \\ C_{20}H_{8} + 2NO_{4} &= C_{20}H_{7}NO_{4} + HNO_{4}, \end{aligned}$$

Bisulphochloride of Ethylene.

Although, as before shown,* ethylene and bisulphide of chlorine are without appreciable action on one another under ordinary circumstances of temperature, etc., and although a temperature of 139° C., effects a disintegration of the ethylene-molecule†.

I have again sought to unite the two directly, because the resulting body, if it resemble its amylene-isotype, would give rise to a highly important series of derivatives.‡ If bichloride of sulphur be exposed in a stoppered bottle in an atmosphere of dry ethylene to direct sunlight, the two unite slowly but almost completely, hydrochloric acid however being liberated.

If a few grammes of bisulphide of chlorine be placed in a well-stoppered bottle which is then filled by displacement with ethylene, the waxed stopper inserted and covered with sheet-caoutchouc, and the whole be completely immersed for twenty hours in boiling water, very complete absorption is found to have taken place on opening the bottle, while only a trace of hydrochloric acid is formed. The bottle may be then refilled with ethylene and the same operation repeated three or four times. The resulting product is then shaken up with warm water, dried, digested with ether, filtered, evaporated *in vacuo* till the ether is expelled, dissolved again in a minimum of ether filtered, and evaporated *in vacuo*.

	grm.		grm.		grm.	
I.	0·3058	gave	0·2908	carbonic-acid and	0·1184	water.
II.	0·2197	,,	0·2356	water.		
III.	0·1798	,,	0·2638	chloride of silver.		
IV.	0·2829	,,	0·6934	sulphate of baryta.		

* Niemann. Ann. Ch. Pharm. cxiii. 3; F. Guthrie, *ibid.*
† Chem. Soc. Qu. J. March, 1860.
‡ See Memoir iv.

		Found.		
$C_4H_4S_2Cl$	I.	II.	III.	IV.
C = 25·13	25·93	,,	,,	,,
H = 4·19	4·30	(4·33)	,,	,,
S = 33·51	,,	,,	,,	33·47
Cl = 37·17	,,	,,	36·29	,,
100·00				100·01

This substance is, according to the previously adopted nomenclature, the *bisulphochloride of ethylene*, $C_4H_4.S_2Cl$.

Bisulphochloride of ethylene has a not unpleasant but indescribable smell; its taste is intensely sweet and pungent. Like the bichlorosulphide of ethylene, its annoying effect upon the eyelids is very enduring;* Its colour is a pale yellow; specific gravity 1·346 at 19 C.° Like the previously described chlor-sulphur compounds of the olefines, it is decomposed by heat and gives off an insupportable smell.

In the next communication, I shall describe the action of anhydrous and hydrated oxides upon this substance, and the behaviour of it and its isotype, bisulphochloride of amylene, upon some of the metal-radicles.

XVI.—*Contribution towards the history of Cinnamic Acid.*

By David Howard.

Notwithstanding the experiments of Gerhardt and Cahours, and the subsequent researches of Blyth and Hofmann, the history of cinnamol and its derivatives is far from being complete. To fill up some of the gaps still existing, I engaged in some experiments upon this interesting group of substances. In the prosecution of my enquiry, I had an opportunity of observing some facts, which I beg to lay before the Chemical Society.

Liquid storax treated in the usual way afforded the crude

* A drop placed beneath the tongue destroys the epidermis and causes a soreness which lasts many days.

cinnamic acid for the experiments. For the purpose of purifying it, I adopted the plan recommended by some chemists, of submitting the crude product to careful distillation. To my surprise, a large portion of the distillate came over in the form of a permanent liquid. The smaller portion, which solidified on cooling, was purified by crystallisation and converted into a silver salt. The silver determination gave the following result:

·2090 grm. of the silver-salt left on ignition
·09850 grm. = 47·13 per cent of metallic silver.

The percentage of silver in benzoate of silver being 47·16, it was obvious that the solid distillate consisted of benzoic instead of cinnamic acid. To find whether this benzoic acid was present in the original crude acid, or whether it had been formed by the destruction of cinnamic acid, a portion of the crude acid was recrystallized and converted into a silver-salt.

·5735 grm. of this salt left on ignition
·2500 grm. of metallic silver = 43·59 per cent.

42·37 being the percentage of silver in cinnamate of silver, it could not be doubted that the crude acid employed contained an appreciable admixture of benzoic acid. It was therefore further purified by solution in alcohol and crystallisation by spontaneous evaporation of the solvent, when large regular crystals were obtained, which, on analysis of a new silver-salt, proved to be pure cinnamic acid.

·5170 grm. left ·2190 = 42·36 per cent. of silver
·5085 grm. left ·2150 = 42·28 per cent. of silver.

These numbers coincide with the theoretical percentage of cinnamate of silver.

A careful distillation of this pure acid, afforded, together with a large portion of an oily product, a small quantity of an acid which solidified in the neck of the retort. This acid was converted into a silver-salt and in this form submitted to analysis:—

·2255 grm. left on ignition ·0955 = 42·35 per cent. of silver,
·2165 grm. left on ignition ·0915 = 42·27 per cent. of silver.

The distilled acid was therefore undecomposed cinnamic acid. In other experiments in which the acid was submitted to a still slower distillation, the whole of it was entirely decomposed and converted into liquid products of decomposition.

Thus it would appear that cinnamic acid, contrary to the statements of most Manuals, is decomposed when kept at a boiling heat, and that it can only be distilled even partially unchanged, when very rapidly heated, care being taken to carry over the vapour as quickly as possible by keeping the upper part of the retort at a very high temperature.

In order to find whether cinnamic acid would decompose when maintained for a long period at a somewhat lower temperature, a portion of the acid was sealed up in a glass tube, and heated for several hours to 200° C. in a paraffin bath; no change however took place.

Another portion was similarly heated in presence of water. It remained likewise unchanged, the silver-salt yielding the following percentage:—

·4805 grm. gave ·2040 = 42·45 per cent. of silver.

The fluid which is formed by the action of heat upon cinnamic acid, proved on investigation to be almost pure cinnamol; the boiling point remained constant at 145° C., till the greater part of the liquid had passed over, when the temperature rose rapidly, leaving in the retort a resinoïd mass of *metacinnamol*. By treating the liquid with bromine the characteristic crystalline dibromide of cinnamol was obtained; and by exposing a portion sealed up in a tube to 200°, it was entirely converted into a glassy mass of metacinnamol, which when submitted to a still higher temperature, was reconverted into cinnamol.

These properties identify the oily product of decomposition of cinnamic acid with cinnamol, or what is the same thing, with styrol, although it appears that the tendency to pass into the solid condition is perhaps less marked in this liquid than in styrol, a fact noticed by other observers in cinnamol formed by the usual process. When very carefully heated, cinnamol obtained by the destructive distillation of cinnamlic acid may be almost entirely distilled without the production of the solid modification.

The preceding experiments prove that at a temperature very near its boiling point, cinnamic acid is decomposed into cinnamol and carbonic acid, according to the equation,

$$C_{18}H_8O_4 = C_{16}H_8 + 2CO_2,$$

a decomposition similar to the transformation into benzol and carbonic acid, which benzoic acid undergoes when its vapour is passed through a red hot tube.

The cinnamol thus obtained from cinnamic acid amounts to from a fourth to a third of the acid employed, so that this reaction furnishes a method of preparing cinnamol much more easily and much more copiously than it could be hitherto obtained. Cinnamol obtained in this manner is perfectly free from benzol. It is well known that the liquid obtained by the usual process viz., distillation of cinnamic acid with lime and even baryta, consists of a mixture of hydrocarbons, in which so large a proportion of benzol is present, that some chemical Manuals state the boiling point of cinnamol at 89° C., proving that the proportion of cinnamol in these mixtures is excessively small. The dry distillation of pure cinnamate of lime likewise furnishes cinnamol quite free from benzol, thus affording a remarkable contrast to the behaviour of a mixture of cinnamic acid and excess of lime.

The crude cinnamol obtained from either cinnamic acid or cinnamate of lime, contains a small quantity of a crystalline substance which may be separated from the more volatile cinnamol by distillation with water; the formation of metacinnamol is thus in a great measure prevented, and the substance in question may be extracted from what is left in the retort by alcohol, from which it crystallises. When purified by several crystallisations from boiling alcohol, which dissolves it freely, while cold alcohol retains a comparatively small portion, the crystalline substance presents itself in the form of brilliant pearly scales which on analysis gave the following results:—

I. ·1563 grm. gave ·5341 carbonic acid and ·0992 water.
II. ·2500 grm. gave ·8605 carbonic acid and ·1545 water.

These numbers represent a hydrocarbon $C_{14}H_6$ or a multiple of it,

	Theory		Experiment I.	Experiment II.
C_{14}	84	93·33	93·19	93·76
H_6	6	6·67	7·05	6·86
	90	100·00		

The crystalline substance when gently heated with bromine, gives rise to the formation of a bromine-compound which is only slightly soluble even in boiling alcohol. The hot solution deposits on cooling, minute scales exhibiting a slightly reddish tint. On analysis the following results were obtained:—

I. ·2780 grm. gave ·5060 carbonic acid 0·985 water,
II. ·1915 grm. gave ·2120 bromide of silver,
III. ·2020 grm. gave ·2255 bromide of silver.

The formula $C_{14}H_6Br$ requires the following values which I place in juxtaposition with the experimental numbers :—

	Theory		Experiment		
			I	II.	III.
C_{14} . .	84	49·41	49·64	——	——
H_6 . .	6	3.53	3.68	——	——
Br . .	80	47·06	——	47·10	47·50
	170	100·00			

The formation and composition of the bromine-compounds could leave but little doubt that the crystalline hydrocarbon must be represented by the formula $C_{28}H_{12}$.

A hydrocarbon of precisely the same composition, and exhibiting also the general characters of the substance derived from cinnamic acid, was described some years ago by Laurent. He obtained the body which he calls "stilbene," together with another crystalline body, "thionessal," in the destructive distillation of hydride of sulphobenzoïl thus,

$$\underset{\text{Hydride of Sulphobenzoïl}}{8\,C_{14}H_6S_2} = 2C_2S_4 + 6HS + \underset{\text{Stilbene}}{2C_{28}H_{12}} + \underset{\text{Thionessal}}{C_{52}H_{18}S_2}.$$

In order to establish the identity of the two substances, I have prepared a quantity of stilbene, according to Laurent's process In repeating the experiments of Laurent, I observed all the phenomena described by that chemist.

On comparing the stilbene procured in this manner with the crystalline substance obtained from cinnamic acid, it was impossible to doubt their absolute identity. I have nothing to add to Laurent's description, except that stilbene prepared by the dry distillation of either hydride of sulphobenzoïl, or of cinnamic acid, fuses at 125° C.

The transformation of cinnamic acid into stilbene is obviously the result of a destructive process, which does not admit of simple representation in formulæ.

The experiments which I have described were performed in Dr. Hofmann's laboratory.

XVII.—*Action of Sodium upon Iodide of Methyl mixed with Ether.*

By J. A. Wanklyn, F.R.S.E., and F. Buckeisen, Ph.D.

Pure methyl has not yet been obtained. Kolbe's method, viz., electrolysis of an acetate, yields methyl always contaminated by some foreign body, probably oxide of methyl, which cannot be completely removed.

Frankland's method, viz., decomposition of iodide of methyl by zinc, also gives a mixture, which, in this case, consists of hydride of methyl and free methyl. This hydride of methyl, Frankland regards as a secondary product, formed after the gas has left the production tube, and due to decomposition of moisture by some zinc-methyl, with which the gas, as it issues forth, is invariably accompanied.

Bearing this circumstance in mind, we determined to try the action of sodium upon iodide of methyl. Since sodium-methyl cannot be prepared by such a process, we expected to obtain pure methyl. Our expectation was not realized, as will appear in the course of the paper.

The iodide of methyl used in our experiments, boiled constantly at 43° C.

We enclosed in a glass tube some sodium along with a few grammes of iodide of methyl and ether. In order to insure the absence of moisture, we next made a short preliminary digestion in the water-bath. Then we let out the first portion of gas, which was no doubt contaminated with products due to traces of water adhering to the materials employed in the experiment. Afterwards we rescaled the tube, heated again to 100° C., and collected the gas over boiling water. After having stood in contact with water during a night, the gas was analysed according to the method employed by Bunsen.

We give the particulars of the analyses:—

The gas was divided into two portions, one of which was placed in the combustion eudiometer, and the other in the absorption tube.

I.—*In the Eudiometer.*

	Volume	Temperature	Pressure	Volume reduced to 0 C. and 1 meter pressure
Volume of gas taken	72·00	26·9°C.	meter 0·15085	9·8876
Volume after addition of oxygen ..	180·96	27·1°	0·25844	42·547
Volume after addition of air	340·90	26·2°	0·41561	129·28
Volume after explosion	308·54	26 7°	0 38336	107·74
Volume after absorption of CO_2 ..	275·42	25·5°	0·378	95·221
Volume after addition of Hydrogen ..	375·0	26·7°	0·4717	161·13
Volume after explosion	252·98	27·3°	0 3575	82·23

II.—*In the absorption tube.*

	Volume	Temperature	Pressure	Volume reduced to 0°C. and 1 meter pressure
Volume of gas taken	93·70	26·9°	meter 0·65305	55·706
Volume after the action of potash and pyrogallic acid	90·63	26·6°	0·6731	55·591
Volume after the absorption of olefines	82·8	25·5°	0·6675	50·551

Some gas after the removal of CO_2, oxygen and olefines, was transferred from the absorption tube to the eudiometer. Its analysis gave the numbers following:—

III.—*In the Eudiometer.*

	Volume	Temperature	Pressure	Volume reduced to 0°C. and 1 meter pressure
Volume taken	84·32	26·7°C.	meter 0·16676	12·809
Volume after the addition of oxygen ..	399·36	26·7°	0·48686	177·12
Volume after explosion	364·95	27·8°	0·45242	150·11
Volume after the absorption of carbonic acid	330·25	25·1°	0·4463	134·99

Another analysis of the same gas yielded :—

IV.—*In the Eudiometer.*

	Corrected at 0° C. and one meter pressure
Volume taken	10·365
Volume after the addition of oxygen	160·75
Volume after explosion	138·40
Volume after absorption of CO_2	125·60

A third analysis of the same gas gave :—

V.—*In the Eudiometer.*

	Corrected at 0° C. and one meter pressure
Volume taken	18·037
Volume after the addition of oxygen	85·611
Volume after the addition of air	198·04
Volume after explosion and absorption of CO_2	137·05
Volume after addition of hydrogen	258·67
Volume after explosion	114·73

Analysis II. shows that the gas was free from carbonic acid and oxygen. It also shows that 55·706 volumes of the gas contained 5·155 vol. of olefines.

In percentage C_nH_n . .	9·3
Gas freed from C_nH_n . .	90·7
	100·0

Analysis I. shows that 9·8876 vols. of gas contain 0·368 vol. of nitrogen. In percentage nitrogen = 3·7.

Analysis V. of the gas free from C_nH_n shows that 18·037 vols. contain 0·21 vol. of nitrogen, or 90·7 vols. contain 1·05 vols. of nitrogen. But 100 vols. of the original gas contain 90·7 vols. of gas free from C_nH_n. Therefore, 100 vols. of the original gas contain 1·05 vols. of nitrogen.

The determination of nitrogen at the end of a hydro-carbon gas analysis is subject to a little irregularity, inasmuch as the small quantities of air introduced in the course of the analysis, tell in the aggregate upon the final nitrogen determination.

Adopting the mean of our two results, we have 2·4 for the percentage of nitrogen.

From Analysis I. we obtain :—

		In percentage.
Original gas . . .	9·8876	100·0
Nitrogen . . .	0·237	2·4
Combustible gas . .	9·6506	97·6
Oxygen consumed . .	24·4084	246·9
Carbonic acid formed .	12·519	126·6

Analyses III., IV., and V., all of the residual gas after removal of C_nH_n give :—

	III.	IV.	V.	Mean.
Combustible gas .	12·507	10·091	17·560	88·3
Oxygen burnt .	29·623	25·059	43·430	215·7
Carbonic acid formed	15·120	12·80	—	109·1

To arrive at the condensation of the olefines we make use of the following data :—

100 vols. of the original gas are composed of,

9·3 vols. of C_nH_n.
2·4 vols. of nitrogen.
88·3 vols. of residual hydro-carbon.

And on combustion furnish,

246·9 vols. oxygen consumed.
126·6 vols. carbonic acid.

88·3 vols. of the residual hydro-carbon gas furnish

215·7 vols. oxygen consumed.
109·1 vols. carbonic acid.

Hence the 9·3 vols. of C_nH_n furnish

31·2 vols. oxygen consumed.
17·5 vols. carbonic acid.

The C_nH_n, therefore, has the condensation of ethylene, which requires,

Vol. taken . .	1·0
Oxygen burnt .	3·0
Carbonic acid .	2·0

With so low a percentage of C_nH_n as is present in the gas under examination, great accuracy in the determination of its condensation is not to be expected; the very indirect manner of arriving at the result having the effect of concentrating the errors of the whole analysis upon the small percentage of olefine.

The 88·3 vols. of hydro-carbon must consist, for the most part, of marsh gas. Some other more complex hydro-carbon is also present; but what other, cannot be revealed by a mere combustion analysis. If the hydro-carbon be very complex, then the percentage of marsh gas must be high; if less complex, then the percentage of marsh gas falls.

Assuming that the accompanying hydro-carbon is methyl, in which case the proportion of marsh gas reaches its lowest, we have for the composition of the gas

C_4H_4 . . .	9·3
Nitrogen . .	2·4
Hydride of methyl .	65·0
Methyl . . .	23·3
	100·0

As is well known, a combustion cannot distinguish marsh gas from a mixture in equivalent quantities of methyl and hydrogen.

That our marsh gas was such a mixture, was highly improbable. Direct proof we have nevertheless sought in another experiment.

We made a fresh quantity of gas, collected it over strong alcohol (previously boiled) and shook it up therewith. Since methyl is very much more soluble in alcohol than is hydrogen, the gas discharged from this alcohol by boiling, should have been very rich in methyl. After washing with water, however, it yielded on combustion numbers agreeing with the composition of hydride of methyl, viz.:—

Contraction.		Carbonic Acid.
10·31	:	5·27

Hydride of methyl requires contraction to carbonic acid in the ratio of 2 : 1.

This gas also contained hardly any olefine, viz., only 2·7 per cent.

We have thus established the following conclusions:—

At 100° C. sodium decomposes iodide of methyl in presence of dry ether, yielding a large quantity of hydride of methyl.

The equation expressing the production of the hydride is neither of the following:—

$$Na_2 + 2(C_2H_3I) = 2NaI + C_2H_2 + C_2H_4$$
$$Na_4 + 4(C_2H_3I) = 4NaI + C_4H_4 + 2(C_2H_4)$$

because, the amount of C_nH_n is too small for the hydride of methyl.

What the product, complementary to the hydride of methyl, really consists of, we have not yet been able to determine.

In conclusion we have to add that we have repeated the experiment and obtained similar results to those which we have described in the paper. With potassium likewise the same peculiarity has been observed as with sodium.

The further investigation of the subject will be made by one of us.

XVIII.—*On the Composition of the Aqueous Acids of constant Boiling Point.*

By Henry Enfield Roscoe.

It is still a very generally received opinion, that a liquid which boils unchanged at a fixed temperature must be regarded as a chemically homogeneous body. This supposition is not, however, borne out either by theoretical considerations or by practical experience.

The proportions in which the constituents of a mixed liquid pass, on boiling, into the state of vapour depend upon the proportions in which the constituents are contained in the liquid, and upon the separate tensions of the vapours of these constituents at the temperature of ebullition. Although the laws which regulate the vaporization of mixed liquids are as yet far from being understood, it is easy to see that the relations between the several tensions and the proportions by weight of the two or more constituents may be such that, at a given temperature of ebullition, the composition of the vapour is identical with that of the liquid. As soon as this point is reached, the mixed liquid boils at a constant temperature without undergoing any change of composition, and in this respect does not differ from a uniform chemical combination. Such mixed liquids possess, however, other properties, by means of which they can be easily distinguished from definite chemica lcombinations. The characteristics by which a chemical compound is recognized, are generally considered to be (1), that the components of such a combination are united in quantities represented by some simple atomic relation; and (2), that this relation remains unaltered under a certain change of physical conditions.

From the experiments of Dalton, Mitscherlich, Millon, Bineau, and others, it has been hitherto supposed that most of the aqueous acids, and especially hydrochloric, hydrobromic, hydriodic, hydro-fluoric, nitric, and sulphuric acids, of very various degrees of strength, not only attain a fixed composition when boiled under the ordinary atmospheric pressure, but that the liquids thus prepared are definite chemical compounds of acid and water. In the present communication, my aim will be to show that this latter supposition is incorrect; that although liquids possessing constant

composition are obtained by boiling the above-mentioned acids under the ordinary atmospheric pressure, these bodies cannot be regarded as definite hydrates, but that the phenomenon of constant composition and fixed boiling-point is to be ascribed to the establishment of that particular relation between the weights and tensions of the constituents, by virtue of which acid and water are contained in the vapour in the same proportions in which they are present in the liquid. I shall show, in the first place, that the composition of the acids obtained by ebullition under the ordinary atmospheric pressure, does not, in the case of any of the acids examined, with one exception, agree with that of a simple hydrate; and, secondly, that in every case when these constant acids are brought under other physical conditions, such as when boiled under different pressures, or when a current of dry air is passed through them at different temperatures, they are decomposed and attain a different but constant composition, so that a mixture of acid and water may be made which, on vaporization at a given temperature, does not undergo any alteration in composition.

1. *Nitric Acid.*

Dalton was the first clearly to point out that mixtures of nitric acid and water, when boiled, undergo such a change that the weak mixtures lose water, and the strong mixtures lose acid, until the residual liquid attains a specific gravity of 1·42, and boils, under the ordinary atmospheric pressure, steadily at 120° C. This observation has since been confirmed by the experiments of Mitscherlich, Bineau, Millon, and Smith. The residual acid obtained by boiling either a weaker or a stronger acid was found by these chemists to possess an almost constant composition, the analyses giving an amount of nitric acid (HNO_6) varying from 66 to 70 per cent. on the liquid. From his own experiments Mitscherlich concluded, that this acid of constant boiling point contains 4 atoms of water to 1 atom of HNO_6, whilst Bineau and others supposed that this acid consists of 3 atoms of water and 1 of nitric acid (HNO_6), corresponding to the well-known series of magnesian nitrates of the formula RNO_6+3HO.

Owing to the discrepancy in these statements, it appeared of interest to determine, as accurately as possible, in the first place, whether the acid obtained by distillation under the ordinary

atmospheric pressure has a constant composition; and, secondly, whether the relation between acid and water is one capable of expression in simple numbers. For this purpose, a quantity of strong acid was prepared by the usual processes,* and freed completely from lower oxides of nitrogen by passing a current of dry carbonic acid through the warm liquid. The acid thus prepared was perfectly colourless, and free from every trace of chlorine and sulphuric acid. The method of determination adopted, consisted either in volumetric analysis with a standard solution of caustic soda of exactly known strength, or in neutralizing the acid with a weighed quantity of pure fused carbonate of sodium, boiling the solution, and adding a small quantity of test acid or alkali to reach the exact point of neutrality, which was supposed to be attained when the litmus became blue. The quantity of acid employed for each determination was such, that the maximum analytical error, the amount of which was determined by control experiments, never attained 0·2 per cent. on the liquid. In order to check the two methods employed, an acid, which with test alkali was found to contain 68·00 per cent. of HNO_6, and with pure carbonate of sodium gave 68·02 per cent. of HNO_6, was neutralized with freshly precipitated carbonate of barium, the barium in solution being estimated as sulphate; 1·3368 grms. of the nitric acid yielded 1·6815 grms. of sulphate of barium, corresponding to 67·95 per cent. of HNO_6.

The composition which aqueous nitric acid of various degrees of strength attains when boiled under the ordinary atmospheric pressure, was determined by diluting portions of the pure concentrated acid to a given extent with water, and, after analysis, distilling them in a small retort, the strength of the residual liquid being then accurately estimated. The experimental results are contained in the following Table, in which Column I gives the volume of acid employed; Column II, the percentage quantity of real acid (HNO_6) contained in the liquid before distillation; Column III, the volume of liquid remaining in the retort; and Column IV, the percentage quantity of real acid (HNO_6) contained in the residual liquid after distillation.

* Millon's statement respecting the difficulty of separating from the distillate the sulphuric acid used for concentrating the nitric acid was not confirmed. Strong nitric acid was easily obtained free from every trace of either sulphuric or hydrochloric acid.

TABLE 1.

No.	I.	II.	III.	IV.
(1)	25 cbc.	99·8	5 cbc.	95·8
(2)	25 ,,	95·2	5 ,,	84·8
(3)	25 ,,	84·7	5 ,,	71·8
(4)	120 ,,	77·8	20 ,,	69·1
(5)	180 ,,	74·7	8 ,,	68·1
(6)	120 ,,	70·5	20 ,,	68·6
(7)	90 ,,	70·5	15 ,,	68·6
(8)	120 ,,	65·1	30 ,,	68·0
(9)	120 ,,	65·1	20 ,,	68·3

From these experiments it is seen, that nitric acids of widely different degrees of concentration attain on boiling a composition varying from 68 to 69 per cent. of real acid. The slight differences in the composition of the residue here observed, arise from the impossibility of performing the experiments under the same physical conditions, as overheating the vapour, unequal exposure to air, &c., cannot be avoided. This is proved by comparing the results of a second series of experiments, detailed in Table 2. The distillation was, in these instances, effected in a small bulb-tube retort, blown before the lamp, in which the ebullition in presence of platinum proceeded more regularly and quietly than in the larger retort before employed; the liquid was also reduced by boiling to the same volume in every experiment, and thus the causes of variation as much as possible avoided. The designation of each column remains the same as in Table 1.

TABLE 2.

No.	I.	II.	III.	IV.	
(1)	20 cbc.	70·2	5 cbc.	68·1	
(2)	20 ,,	68·3	5 ,,	68·0	
(3)	20 ,,	68·3	5 ,,	67·9	
(4)	20 ,,	66·9	5 ,,	68·0	
(5)	20 ,,	66·2	5 ,,	68·0	
(6)	20 ,,	66·2	5 ,,	68·0	Mean 68·00

Hence we may conclude:—

(1.) That the residual liquid obtained by boiling aqueous nitric acid of various degrees of concentration under the ordinary atmospheric pressure possesses a constant composition.

(2.) That the liquid thus obtained contains 68·0 per cent. of real acid, and that, therefore, the proportion between acid and water cannot be represented by any simple atomic relation, the formula $HNO_6 + 3HO$ requiring 70·0 per cent. of HNO_6.*

The boiling-point of the acid, containing 68·0 per cent., was found to be 120°·5 C., under a barometric pressure of $0^{m}·735$; its specific gravity at 15°·5 C. was shown to be 1·414 as a mean of two determinations.

Distilled at other temperatures, the relation of real acid to water will, if the phenomenon of constant boiling-point depends altogether on physical causes, be found to be a different one. In the following experiments, aqueous nitric acid of various degrees of strength, was distilled under diminished atmospheric pressure, effected by placing the acid in a retort, the neck of which, drawn out and bent at an acute angle, passed through a solid caoutchouc stopper into a large bolt-head of 20 litres capacity, furnished with a divided manometer-tube, and communicating with the cylinder of a large air-pump. By this means the acid could be distilled under any wished-for pressure less than that of the atmosphere; by cooling the bolt-head, and by having a large absorbent surface of caustic soda in the interior of the flask, it was easy to keep the mercury in the manometer tube to within 5 millimetres of the required height during the whole course of the distillation. Table 3 contains the results of a series of such experiments; Column I, gives the pressure in millimetres of mercury, under which the distillation took place (*i. e.*, the barometric pressure,— the height of the mercurial column in the manometer-tube); Column II, the volumes of liquid employed; Column III, the percentage of real acid contained in this liquid; Column IV, the volume remaining after distillation; Column V, the percentage of real acid contained in the residual liquid.

* Calculated percentage composition of the hypothetical hydrates of nitric acid:—

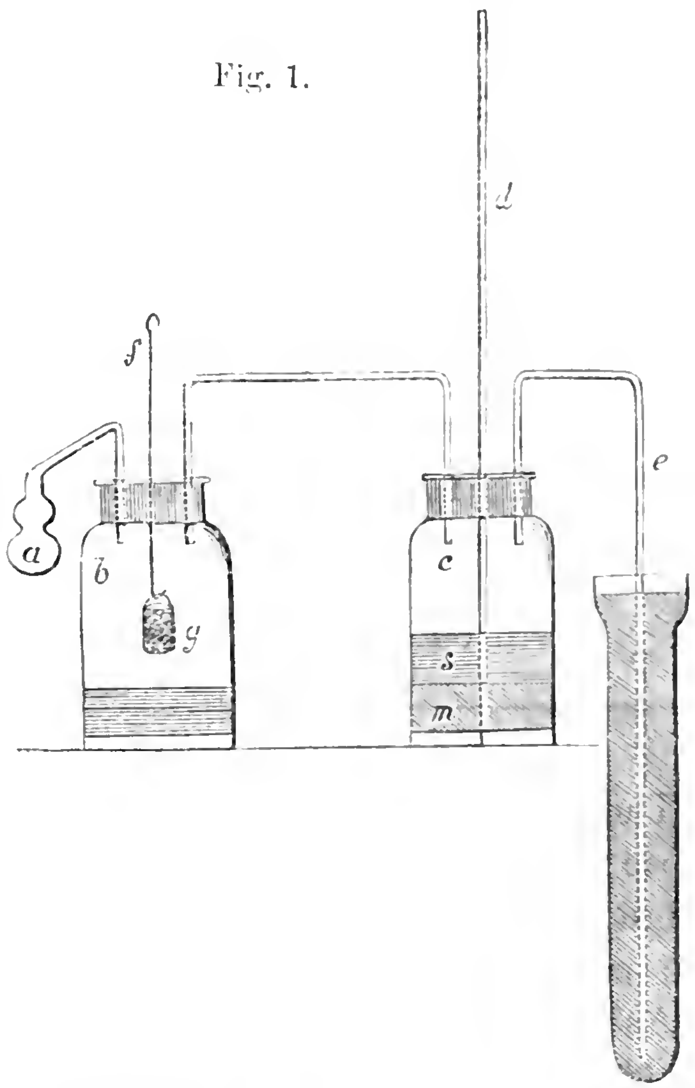
	(1st)	(2nd)	(3rd)	(4th)
$H.NO_6$ . .	87·5	77·8	70·0	63·6
HO . .	12·5	22·2	30·0	36·4
	100·0	100·0	100·0	100·0

TABLE 3.

No.	I.	II.	III.	IV.	V.
(1)	75 mm.	150 cbc.	69·9	50 cbc.	66·7
(2)	50 „	20 „	68·3	5 „	67·2
(3)	75 „	150 „	66·9	50 „	66·7
(4)	68 „	20 „	66·5	5 „	66·8
(5)	75 „	20 „	66·2	5 „	66·5
(6)	75 „	120 „	65·1	30 „	66·7
(7)	150 „	150 „	66·9	50 „	67·6

Although showing a maximum difference of 1 per cent., owing to the acid being mechanically carried over by the irregular percussive ebullition, which it is impossible to prevent when nitric acid is heated under a diminished pressure, the results obtained are still sufficiently accurate to prove, that under a pressure of about 70 millimetres of mercury, when the boiling-point lies between 65° and 70°, a liquid possessing a constant mean composition of 66·7 per cent. of HNO_6 is obtained, whilst under a pressure of 150 millimetres, the equilibrium occurs when the percentage of acid reaches 67·6.

Fig. 1.



The distillation of nitric acid under pressures greater than that of the atmosphere, is accompanied by considerable experimental difficulties, owing to the impossibility of bringing the acid into contact with mercury. These difficulties were overcome by employing the following arrangement:—The bulb-retort (a) Fig. 1,

containing the acid, was connected by means of a solid caoutchouc stopper with a strong bottle (*b*), of one litre capacity, containing some dilute nitric acid; through the stopper passes a second tube, communicating with another similar bottle (*c*) containing mercury (*m*) and a strong solution of caustic soda (*s*); a divided manometer tube (*d*) dipped into the mercury, and a third tube (*e*) passing through the stopper of the bottle (*c*) could be placed to any required depth into a reservoir of mercury. The bottle (*b*) being immersed in cold water, the increase of pressure was attained by pushing the glass bucket (*g*), filled with pieces of marble, into the dilute acid, by means of the stiff iron wire (*f*), working perfectly air-tight through the caoutchouc stopper. As soon as the mercury in the manometer tube had attained the wished-for height, and the gas issued from the extremity of the tube (*e*) under the mercury, a portion of the acid in the retort was distilled over, and the residue afterwards analyzed. By withdrawing the marble from the acid and again immersing it when required, the pressure was kept tolerably constant during the whole course of the experiment. The numbers in the following Table show, that distilled under a mean pressure of 1,220 millimetres of mercury, beyond which it was found inconvenient to operate, the composition of the residual liquid reached 68·6 per cent. of real acid, being a deviation from the acid distilled under ordinary pressures of 0·6 per cent.

TABLE 4.

No.	I.	II.	III.	IV.	V.
(1)	1260 mm.	20 cbc.	70·5	5	68·8
(2)	1210 „	20 „	68·3	5	68·7
(3)	1190 „	20 „	68·0	5	68·4

Mean 1220. Mean 68·6

The numbers in the columns have the same signification as those in Table 3, except in the first, in which the sum of the heights of the barometric column and the column of mercury in the manometer tube is given.

As it has thus been shown that aqueous nitric acid is a liquid which does not give rise on distillation to bodies possessing a simple atomic constitution, but that for each temperature a liquid

having a constant composition is obtained, it appeared of interest to determine for lower temperatures the composition of the acid unalterable by vaporization.

For this purpose, air, completely dried over sulphuric acid and phosphoric anhydride, was passed through the nitric acid contained in the burette-shaped vessel, Fig. 2, until no further change in composition was observed. The requisite temperature was obtained by immersing the burette in a large water-bath, the heat of which was kept constant, a weighed U-tube, containing phosphoric anhydride, being placed between the burette and the drying apparatus, to ensure all absence of moisture. Experiments thus conducted for every temperature, show that a point is reached at which the composition of the aqueous acid undergoes no further change by vaporization. In Table 5, Column I gives the percentage of real acid in the liquid before the experiment; Column II, the percentage after the experiment; Column III, the fraction of the original volume of acid remaining after the experiment; Column IV, the duration of the experiment in hours.

Fig. 2.

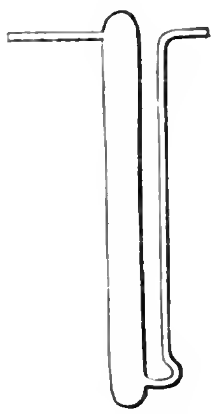


TABLE 5.

Passage of dry air through acid at 100° C.

No.	I.	II.	III.	IV.
(1)	68·0	66·2	$\frac{1}{4}$	2 hrs.
(2)	64·9	66·1	$\frac{2}{3}$	1 ,,
(3)	64·9	66·3	$\frac{1}{4}$	3 ,,

Passage of dry air through acid at 60° C.

No.	I.	II.	III.	IV.
(1)	68·0	66·9		6 hrs.
(2)	66·9	65·7		9 ,,
(3)	65.7	65·2	$\frac{1}{2}$	30 ,,
(4)	65·2	64·9		9 ,,
(5)	64·9	64·8		20 ,,
(6)	64·9	64·8	$\frac{3}{4}$	8 ,,
(7)	64·8	64·5	$\frac{1}{2}$	9 ,,
(8)	64·5	64·4	$\frac{1}{3}$	9 ,,
(9)	64·0	64·5	$\frac{1}{2}$	8 ,,
(10)	64·5	64·5	$\frac{1}{4}$	6 ,,

Passage of dry air through acid at mean temp. of 13° C.

No.	I.	II.	III.	IV.
(1)	68·0	66·2		48 hrs.
(2)	66·2	65·2		24 „
(3)	65·2	64·0	$\frac{1}{2}$	24 „
(4)	64·0	64·0		48 „
(5)	64·0	64·0		24 „
(6)	63·0	63·3		48 „
(7)	63·9	63·9		72 „
(8)	63·9	64·0		48 „

It is thus seen—(1.) That weak or strong aqueous nitric acid through which dry air is passed at 100°, attains a constant composition of 66·2 per cent. of real acid. (2.) That when air is passed through the same acid at 60°, the composition becomes constant at 64·5 per cent.; and (3.) That at the ordinary atmospheric temperatures—in mean 13°—the equilibrium is reached when the liquid contains 64·0 per cent. of real acid.

The ease with which strong nitric acid is decomposed, even at temperatures below its boiling point, is well known. It seems to be impossible to prepare the real acid HNO_6 by employing the usual method of distillation, rectification over sulphuric acid, and volatilization of the oxides of nitrogen by means of a current of dry air or carbonic acid. None of the chemists who have worked upon this subject appear to have had the real acid, and I have also failed to obtain it, although every care to ensure absence of moisture was taken; one colourless acid contained 99·8 per cent. of real acid, another 99·47 per cent. The former, nearly anhydrous acid, not only suffered decomposition on boiling, as is seen by reference to Table 1, but underwent alteration when a current of air perfectly dried over a large quantity of phosphoric anhydride was passed through the liquid at 15°. In seven hours, after which time three-fourths of the acid had been volatilized, the percentage of real acid had sunk to 98·77. This shows that nitric acid (HNO_6) undergoes decomposition, not only when vaporized at the boiling point, but also at the ordinary atmospheric temperatures.

II.—*Sulphuric Acid.*

We owe to Marignac the interesting and important observation, that real sulphuric acid (HSO_4) cannot be obtained by the

distillation either of a weaker aqueous acid or of a stronger fuming acid. The real acid can only be prepared by crystallisation, and, on boiling, is decomposed into anhydride, which is seen in the receiver, and a weaker acid remaining in the retort. Marignac showed that this weaker residual acid boils at 338° C, without undergoing change; and he further proved that aqueous sulphuric acid of every degree of concentration, whether containing more or less water than the real acid (HSO_4), attains this constant composition on boiling. From four separate determinations, Marignac found that this residual liquid contained 98·70 per cent. of real acid.

The following determinations have confirmed in every particular Marignac's conclusions. The analyses were made by weighing out the requisite quantities of pure fused carbonate of sodium, the exact point of neutrality being estimated by addition of small volumes of standard alkali and acid of well-established strengths.

(1.) Pure strong sulphuric acid, containing 93·4 per cent. of real acid, was distilled in a retort, until two-thirds of the liquid had been volatilized. The liquid remaining in the retort contained 98·7 per cent. of real acid.

(2.) An acid containing 98·37 per cent. of HSO_4 was distilled in a small retort, until one-fifth of the original volume remained. The residue contained 98·32 per cent. of HSO_4.

(3.) An acid containing 98·37 per cent. of HSO_4 was boiled down in a porcelain capsule to one-third of its original volume. The residual liquid contained 98·45 per cent. of real acid.

(4.) An acid containing 100·33 per cent. of HSO_4, and fuming in contact with the air at ordinary temperatures, was boiled down to one-eighth of its orignal volume. The residual liquid contained 98·8 per cent. of real acid.

(5.) Another portion of the same fuming acid, which a second analysis showed to contain 100·34 per cent. HSO_4, was boiled to one-fourth of its original volume. The residual liquid contained 98·40 per cent. of real acid.

It thus appears not only that aqueous sulphuric, like aqueous nitric acid, attains an unalterable composition not corresponding to any definite hydrate, on distillation under the ordinary atmospheric pressure; but we also notice, what is very remarkable, that both the real acids, HNO_6 and HSO_4, bodies which possess in other respects the characteristics of well-defined chemical com-

pounds, are decomposed on boiling, yielding that aqueous acid which remains unchanged at the temperature of ebullition.

III.—*Hydrochloric Acid.*

Bineau found that aqueous hydrochloric acid boiled under the ordinary atmospheric pressure, attained a composition of 20·2 p.c. of HCl, corresponding exactly to the formula $HCl + 16HO$, and this liquid he conceived to be a definite hydrate. In a research upon the absorption of hydrochloric acid and ammonia in water, published in vol. XII, page 128, of the Journal of the Chemical Society, which I made in conjunction with Mr. Dittmar, this result of Bineau's was, to a certain extent, confirmed, inasmuch as the acid of constant composition obtained by ebullition under the ordinary atmospheric pressure was found to contain 20·24 per cent. of HCl; but it was at the same time shown, that distilled under other pressures, or vaporized at other temperatures, this acid was decomposed, other liquids of constant composition being then produced, and the conclusion was therefore drawn that this hydrate has no real existence. The following Table 6, extracted from the above-mentioned memoir, gives the relation between the pressure under which the acid is distilled, and the composition of the constant liquid. The Column P shows the pressure in metres of mercury, under which aqueous hydrochloric acid must be distilled to attain the constant composition given in the next column.

TABLE 6.

Pm.	Percentage of HCl.	Pm.	Percentage of HCl.	Pm.	Percentage of HCl.	Pm.	Percentage of HCl.
0·05	23·2	0·6	20·7	1·3	19·3	2·0	18·5
0·1	22·9	0·7	20·4	1·4	19·1	2·1	18·4
0·2	22·3	0·76	20·24	1·5	19·0	2·3	18·3
0·3	21·8	0·8	20·2	1·6	18·9	2·4	18·1
0·4	21·4	0·9	19·9	1·7	18·8	2·5	18·0
0·5	21·1	1·0	19·7	1·8	18·7		
		1·1	19·5	1·9	18·6		
		1·2	19·4				

Hence it is evident:—(1.) That there exists for each pressure a corresponding aqueous hydrochloric acid, which undergoes no change in composition when distilled under this pressure, and therefore has a constant boiling point. (2.) That the composition of these aqueous acids is different for each pressure, a gradual change in pressure being accompanied by a gradual alteration in the percentage of hydrochloric acid.

When aqueous hydrochloric acid is vaporized by passing a current of dry air through the liquid at a given temperature, a similar point is reached beyond which no decomposition occurs. Table 7 contains the interpolated values obtained from the experimental results given in the original paper. The first column gives the temperatures; the second column gives the percentage of HCl contained in the acid, unalterable at the corresponding temperature.

TABLE 7.

T°.	Percentage of HCl.	T°.	Percentage of HCl.	T°.	Percentage of HCl.	T°.	Percentage of HCl.
0°	25·0	30°	24·1	60°	23·0	90°	21·4
5°	24·9	35°	23·9	65°	22·8	95°	21·1
10°	24·7	40°	23·8	70°	22·6	100°	20·7
15°	24·6	45°	23·6	75°	22·3		
20°	24·4	50°	23·4	80°	22·0		
25°	24·3	55°	23·2	85°	21·7		

IV. *Hydrobromic Acid.*

Löwig first observed that water saturated at the ordinary atmospheric temperature with hydrobromic acid gas loses acid when boiled, and that water containing but little gas in solution loses water under similar circumstances. Bineau showed that the composition of the acid obtained by boiling was constant, and, his experiments proving that such acid contained from 46·1 to 47·4 per cent. of HBr, he concluded that on distillation the hydrate containing 10 atoms of water is formed. According to theory, this hydrate should contain 47·38 per cent. of HBr, when the equivalent of bromine is taken as 80. On exposing aqueous acid of the above strength in a closed vessel over dried potash, or on passing a current of dry air through the acid, Bineau found that the residual liquid contained from 48·7 to 51·7 per cent. of

hydrobromic acid; this he assumes to be a hydrate containing 9 atoms of water, composed theoretically of equal weights of water and real acid (HBr.)

For the purpose of determining the exact relation of the composition of aqueous hydrobromic acid to the temperature of ebullition, the acid was prepared by shaking together pure bromine, water, and phosphorus, added in small pieces from time to time, until the liquid became colourless, the strong fuming solution being freed by distillation from phosphorus and phosphoric acid. The pure and colourless acid thus prepared was diluted to a given extent with water; and as soon as the percentage of real acid (HBr), which the diluted liquid contained had been estimated by accurate volumetric analysis with silver, it was boiled in a bulb-tube retort, under the ordinary atmospheric pressure, until a certain portion of the acid had distilled over, when the composition of the residue was determined by exact analysis with silver.

In Table 8 are seen the results of eight such distillations with aqueous hydrobromic acids of various degrees of concentration: Column I gives the barometric pressure under which the acid boiled; Column II, the volume in cubic centimetres of acid employed: Column III, the percentage of HBr contained in the original liquid; Column IV, the volume in cubic centimetres of acid remaining in the retort after the distillation; and Column V, the percentage of HBr contained in the residual liquid, being the mean of two analyses, which generally differed only in the second decimal place.

TABLE 8.

No.	I.	II.	III.	IV.	V.
	m.				
(1)	0·752	25 cbc.	45·54	8 cbc.	47·38
(2)	0·752	50 „	45·58	8 „	47·39
(3)	0·753	50 „	47·30	25 „	47 78
(4)	0·762	25 „	47·65	12 „	47 86
(5)	0·753	20 „	47·78	5 „	47·61
(6)	0·752	12 „	47·87	6 „	47·73
(7)	0·752	50 „	49·00	8 „	47·71
(8)	0·762	25 „	49·51	10 „	47·84

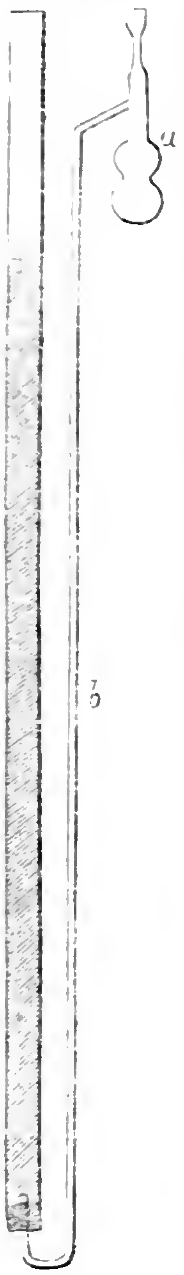
If the distillations are conducted under the same conditions, the compositions of the residual acids are identical (see Nos. 4 and 8); if the physical conditions (barometric pressure, and volume of liquid employed) are different, the acid may vary in composition about 0·1 or 0·2 per cent., as is seen in one or two of the numbers. From the foregoing experiments we see that aqueous hydrobromic acid when boiled under the ordinary atmospheric pressure of 0·76 of mercury, attains a fixed composition of 47·8 per cent. of real acid, or contains 0·5 per cent. more acid than Bineau's hypothetical hydrate. Under these circumstances it was found to boil constantly at 126°C. That the point of constant composition which aqueous hydrobromic acid attains on vaporization, is not solely dependent upon chemical attractions, but is mainly influenced by physical circumstances, is still more distinctly seen on examining the change which the aqueous acid undergoes when a current of dry air is passed through the liquid at a constant temperature. Through a liquid containing 47·65 per cent. of real acid, dry air was passed at the temperature of 16° for 50 hours; after the lapse of this time, the strength of the acid reached 51·8 per cent., and after the air had passed for 30 hours longer, the liquid contained 51·65 per cent. of real acid as a mean of two analyses, and had, therefore, attained the point of constant composition. Hence it is clear that neither of the supposed hydrates of hydrobromic acid has a real existence. In order to determine the point of equilibrium for other temperatures, perfectly dry air was passed through the acid at 100° contained in the burette Fig. 2, and the alteration which the liquid underwent was determined. The following results were obtained :—

Dry air passed through aqueous acid at 100° C.

											P.C. real acid.
(1)	1 vol. acid	containing	48·0	p. c.	when reduced to	$\frac{1}{8}$	vol.	contained	49·59
(2)	"	"	48·05	"	"	$\frac{2}{3}$	"	"	49 07
(3)	"	"	49·10	"	"	$\frac{1}{2}$	"	"	49·35
(4)	"	"	50·10	"	"	$\frac{1}{3}$	"	"	49·35

The aqueous acid was also distilled under a greatly increased pressure by help of the arrangement represented in Fig. 3. (*a*) Fig. 3 is a small bulb blown before the lamp, to which is fused the glass tube (*b*), communicating by a solid caoutchouc stopper with

Fig. 3.



the divided manometer tube (c), containing mercury. After the tube (c) had been filled with mercury to the requisite height, the acid was placed in the bulb, and then the drawn-out end closed before the blowpipe. The distillation was now commenced and continued until the acid had diminished to a given volume, when the pressure was read off from the difference of height of the columns of mercury in the two tubes. For the purpose of obtaining the boiling point of the acid under these circumstances, a thermometer was inserted into the bulb-tube, and the apparatus made air-tight by a joint of caoutchouc and lead-foil carefully wrapped with copper-wire. Under a total pressure of 1·952 metres of mercury, the acid boiled at 153° C; analysis of the residual acid gave the following results :—

(1) Acid containing 48·0 per cent. left after distillation a residual liquid containing 46·30 per cent. of real acid (HBr).

(2) Acid containing 46·07 per cent. left after distillation a liquid containing 46·36 per cent. of real acid.

v. *Hydriodic Acid.*

Bineau concluded that the liquid of constant boiling point obtained by distilling a diluted or a saturated aqueous solution of hydriodic acid was composed of 11 atoms of water to one of real acid (HI). The residual acid contained, according to his experiments, from 56·3 to 57·2 per cent. of hydriodic acid, whilst, according to calculation, the 11-atom hydrate requires 56·39 per cent. of real acid. Aqueous hydriodic acid was prepared by leading into distilled water the gas evolved by heating a mixture of 20 parts of pure iodine, 14 parts of iodide of potassium and 1½ parts of phosphorus mixed with a little water. The acid thus obtained of any requisite degree of concentration was perfectly colourless when preserved out of contact with air, and although the acid was always distilled in a current of hydrogen, it still became slightly

coloured, but was not decomposed to such an extent as to affect the results of the analysis. The composition of the acid before and after the distillation was determined by volumetric analysis with silver; the results of these determinations, as is seen by reference to the following numbers, are closely concordant; care, however, must always be taken to have excess of silver present at the commencement of the analysis, otherwise some iodine is liberated by the free nitric acid.

TABLE 9.

Distillation of aqueous hydriodic acid under the ordinary atmospheric pressure.

Volume of liquid employed in each experiment 25 cbc.

„ „ remaining after each distillation 13 cbc.

	Percentage of real acid taken.	Percentage of real acid in the residue.
(1)	56·50	57·03
(2)	56·70	56·93 56·94 56·90
(3)	57·24	57·03
(4)	57·17	57·16 57·03 57·12
(5)	58·76	57·03 57·10

Hence it is seen that the acid of constant composition which is obtained when aqueous hydriodic acid is boiled under the ordinary atmospheric pressure, contains 57·00 per cent. of real acid, and cannot, therefore, be considered to be a definite hydrate of hydriodic acid. The boiling point of this acid was found to be 127° C. under a barometric pressure of 0·774 metre. In order to ascertain the point of equilibrium for other temperatures, aqueous hydriodic acid was vaporized in a current of dry hydrogen gas at the temperatures of 16° and 100°. Table 10 gives the results of such experiments.

TABLE 10.

Vaporization of aqueous hydriodic acid in a current of dry hydrogen at ordinary atmospheric temperature.

	Temp.		Duration of the experiment.		Percentage of real acid taken.		Percentage of real acid in residue.
(1)	15°	..	32 hours	..	57·0	..	59·44
(2)	15°	..	41 ,,	..	59·44	..	60·36 60·33
(3)	17°	..	15 ,,	..	60·03	..	60·27
(4)	17°	..	15 ,,	..	60·27	..	60·42 60·39
(5)	19°	..	10 ,,	..	60·21	..	60·68
(6)	19°	..	6 ,,	..	60·68	..	60·49 60·42

Vaporization of aqueous hydriodic acid in a current of dry hydrogen at 100° until half the liquid was volatilized.

	Percentage of real acid taken.				Percentage of real acid in residue.
(1)	56·98	..	..	..	58·49
(2)	59·78	..	..	..	58·26
(3)	58·21	..	..	..	58·24 58·20

VI. *Hydrofluoric Acid.*

Aqueous hydrofluoric acid, when boiled under the ordinary atmospheric pressure, attains, according to BINEAU, a constant composition corresponding to the formula $HFl + 4HO$, and containing 35·9 per cent. of anhydrous acid.

In order to verify this assertion, pure aqueous hydrofluoric acid was prepared by leading the gas evolved from a strong acid heated in a platinum retort into water, also contained in a platinum vessel; the acid thus obtained being then boiled under the atmospheric pressure, and the quantity of acid contained in the residual liquid determined, by throwing the acid, weighed in

a platinum capsule, into a vessel containing an excess of standard soda solution. The quantity of free soda was estimated by adding a slight excess of test acid, and the point of neutrality was considered to be reached when the litmus again became coloured blue on adding soda solution drop by drop in the cold. The results of a series of experiments thus conducted are seen in Table 11, in which Column I gives the volume of acid before boiling; Column II the percentage of HFl contained in the liquid before boiling; Column III the volume of HFl after boiling; and Column IV the percentage of HFl contained in the liquid after boiling.

TABLE 11.

I.	II.	III.	IV.
80 cbc.	1·2	6 cbc.	5·8
80 ,,	6·2	40 ,,	11 8
35 ,,	11·8	6 ,,	29·0
80 ,,	16·5	6 ,,	35·4 34·9
20 ,,	32·0	2 ,,	35·2
60 ,,	35·4	30 ,,	36·4 36·2
80 ,,	36·4 36·8	60 ,,	37 0 37·1 37·1
24 ,,	26·5	12 ,,	37·6 37·5

I.	II.	III.	IV.
12 cbc.	36·9	6	37·4 37·2
24 ,,	38·1	12	36·1 36·0
12 ,,	38·1	6	36·8 36·7
24 ,,	38·9	12	38·1 38·2
40 ,,	39·0	20	35·1 36·2 36 1
80 ,,	41·6	40	39·1 39·0

From these experiments it is evident that when aqueous hydrofluoric acid is boiled in platinum vessels under the ordinary atmospheric pressure, it attains a composition varying from 36 to 38 per cent. of HFl. The great differences observed arising from the impossibility of keeping the physical conditions constant, under which the ebullition takes place. We may take the mean 37·0 per cent. as representing pretty closely the composition of the acid unalterable by boiling in the air. If a true chemical compound between acid and water were thus produced, such large

variations in the composition of the residual acid could not have been found. Vaporized at other temperatures, this constant hydrofluoric acid, containing 37·0 per cent. of HFl undergoes change. A portion of acid of the above strength, obtained by ebullition was placed in a platinum crucible over quick lime inside a leaden exsiccator closed with a lid having a sulphuric acid joint. After standing at a temperature of 15° C. for 4 days, the acid was found to contain, in two analyses, 36·4 and 36·6 per cent. of HFl; after remaining 4 days longer at the same temperature, the liquid contained 33·5 per cent. of acid; and when the acid had been standing for 2 more days at the same temperature over quick lime, it was found to contain 32·5 and 32·7 per cent. of acid. A weaker acid was next vaporized under like conditions; an acid containing 31·6 per cent. of HFl placed over quick lime at 15° attained, after 2 days, a composition of 32·1 per cent., and after a further exposure in the exsiccator for 4 days, two analyses showed that it contained 32·4 and 32·3 per cent. of HFl.

I beg to thank my assistant Mr. Schorlemmer for the able help which he has given me in carrying out the foregoing experiments.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

Anniversary Meeting, March 30, 1860.

Professor Brodie, President, in the Chair.

The following REPORT was read by the President:—

The number of Fellows of the Chemical Society has, during the last year, continued to increase; 26 new Fellows have been elected, 3 Fellows have resigned, and three have been removed by death.

At the last Anniversary Meeting, March, 1859,

The number of Fellows was	302
The increase has been	21
The number of present Fellows is . .	323

The number of Associates at the last meeting was 9, and 3 have been since elected.

It appeared desirable to the Council to connect with the Society a greater number of the distinguished Chemists of foreign countries. The number of foreign members has hitherto been limited to 25. Application was made to the Society for power to increase this number to 40. At the present moment, however, it has not been thought expedient to add more than 6 names to the list, making in all 30 Foreign Members. The names thus added are the well-known names of Berthelot, Deville, Frémy, Fritzsche, Mulder, and Peligot.

The Council have ever regarded the formation of a Library of Chemical Works, as one of the most important objects to which the funds of the Society could be devoted, and they are especially desirous to render it at all times accessible and serviceable to the Fellows. They believed that these ends would be promoted by the

appointment of a permanent Librarian; this office has been undertaken by Mr. Watts, a gentleman who is familiar with the literature of the science. Mr. Watts is at present engaged in preparing a new catalogue of the books.

The following papers have been read at the Meetings of the Society, since the Anniversary Meeting of 1859:—

"On the action of Boracic Acid upon the salts of the more volatile acids at high temperatures," by Mr. A. Norman Tate.

"On Boric and Silicic Acids," by Dr. Odling.

"On the action of Hydrochloric Acid upon Sulphide of Mercury in the presence of certain other substances," by Mr. F. Field.

"On the absorption of Ammonia and Hydrochloric Acid by water," by Dr. Roscoe.

"On Bases produced by Nitrous Substitution," by Mr. S. C. Wood.

"On the commercial estimation of Nitre," by Mr. J. S. Blockley.

"On the manufacture of Sulphate of Copper," by Mr. J. S. Blockley.

"On the saline atomic volume of Lithium," by Dr. Odling.

"On the action of Boracic Acid upon the Carbonates of the Alkaline Earths," by Prof. Bloxam.

"On the combination of Potassium with Carbonic Oxide," by Prof. Brodie.

"Remarks on the immediate source of the Carbon exhaled by the lungs," by Dr. Edward Smith.

"On the Crystalline Hydrates of Baryta and Strontia," by Prof. C. L. Bloxam.

"Description of an hermetically sealed Barometer," by Mr. Richard Adie.

"Note on the purification of Esculin and Paviin," by Prof. Stokes.

"On the action of Pentachloride of Phosphorus on Tartaric Acid," by Messrs. Perkin and Duppa.

"On the Vapour-density of Ethylenamine," by Dr. Hofmann.

"On the formation of Starch," by Dr. Moldenhauer.

"On the application of Electrolysis to the detection of the poisonous metals in mixtures containing organic matter," by Prof. Bloxam.

"On the Carbonates of Alumina and the Sesquioxides of Chromium and Iron," by Mr. James Barratt.

"On refining Gold when alloyed with Tin or Antimony, so as to render it fit for the purposes of Coinage," by Robert Warington.

"On certain sources of loss of precious metal in some operations of assaying," by Mr. G. H. Makins.

"On an Iron Sand from New Zealand," by Dr. J. H. Gladstone.

"On the composition of Air from Mont Blanc," by Dr. E. Frankland.

"On Biniodacetic Acid," by Messrs. Perkin and Duppa.

"On some derivatives from the Olefines," by Dr. Guthrie.

"On New Zealand Iron Sand," by Mr. E. Riley.

"On the action of Chloride of Ethyl upon Ammonia," by Mr. Grooves.

The following discourses have been delivered:—

"On Polyatomic Alcohols," by Dr. Debus.

"On Graphite," by Prof. Brodie.

"On Gas Analysis," by Prof. Williamson.

During the present year the Society has lost by death three of its Fellows, Mr. Jacob Bell, Mr. Reginald Morley, and Dr. George Wilson, Professor of Technology at Edinburgh. It is the custom to give a brief account of the lives of those Fellows who are thus lost to the Society.

Mr. Jacob Bell was born in Oxfordshire, in the year 1810. His father was the founder of the important Pharmaceutical establishment with which his name is thus connected, and at 17 years of age he was apprenticed to his father's firm. In the intervals of business he still found time for self-improvement, and attended the lectures on Chemistry at the Royal Institution, and on the practice of Physic at King's College. He had also a decided taste for art, and received lessons on Painting from his friend the Acadamician, Mr. H. P. Briggs. This taste led him in later years to acquire a valuable collection of paintings, chiefly of the artists of the English school. This collection he bequeathed to the British Nation.

As the chief founder of the Pharmaceutical Society, Mr. Jacob

Bell had the strongest claims to the gratitude of his profession and to the consideration of all interested in the application of Chemical science. The foundation of this Society was decided on at a public meeting held upon the 15th of April, 1841; but it was at meetings held at the house of Mr. Jacob Bell, that its constitution may truly be said to have been framed.

He was a member of the Council from the commencement of the Society, and rarely allowed any engagement to interfere with his attendance at its meetings. At his death he was its President. He also founded the Journal of the Pharmaceutical Society and Transactions, to which he made several literary communications, and to the support of which he liberally contributed.

These professional labours were not unappreciated by other countries. Mr. Bell was an honorary member of various foreign scientific societies. He was one of the original Fellows of the Chemical Society, and also a Fellow of the Linnean and Zoological Society, and of the Society of Arts.

With the view of furthering the interests he had so much at heart, Mr. Bell obtained a seat in Parliament, and in June, 1851, he moved for leave to bring in a Bill to regulate the qualification of Pharmaceutical Chemists, and for other purposes connected with Pharmacy, which, although modified in many important respects from its original form, passed into law.

Towards the end of the year 1858, Mr. Bell's health seriously declined. In the year 1854, owing to his exertions in public speaking, he contracted an ulceration of the tongue, from which he never thoroughly recovered. His death took place at Tunbridge Wells, on Sunday, the 12th of June, 1859.

Mr. Bell's was an useful and honourable life. He laboured in the most disinterested manner, for a period of 18 years, to raise the standard of education in his profession, and to advance its true interests. Greatly through his efforts, relations were established between Practical Pharmacy and Scientific Chemistry, which in this country had never before existed, and the importance of which no Fellow of this Society can fail to recognize.

Robert Reginald Ingham Morley was born August 26th, 1826. A love of science, which was early manifested, induced him to enter himself as a student at the Royal College of Chemistry, in 1849, where he continued his studies for several years, and acted as Senior Assistant to Dr. Hofmann during the Winter Session of 1854.

In 1851, he communicated a paper to the Chemical Society "On Propione, the Ketone of Propionic Acid," and in 1854 communicated another paper to the Society (in conjunction with Mr. J. S. Abel) "On the action of Iodide of Ethyl on Toluidine."

He was for some time one of the Visitors of the Royal Institution.

Circumstances led him to give up the study of Chemistry as a profession, and subsequently his declining state of health prevented his making that use of his laboratory which his love of science would have prompted.

He died January 11th, 1860, aged 33.

George Wilson* was born in Edinburgh, on February 21, 1818. His parents, observing his quick sensibility and studious habits, determined to give him the best education in their power, and accordingly he passed through the High School of his native city, entered its University in 1833, and graduated in medicine six years afterwards. During this time, he showed himself a diligent and enthusiastic student of science, and his mind was directed more and more towards chemistry. After spending a session in London as assistant to Professor Graham, now the Master of the Mint, he commenced giving public lectures at Edinburgh. There he was attacked by a severe and lingering illness, from which he only recovered after the amputation of his left foot, and with a constitution so shattered that he never knew afterwards the blessing of sound health; yet he rose from his sick bed, not merely with his former elasticity of spirits and enthusiasm for science, but with a still nobler purpose in life, for thenceforward religion had the supreme control of his thoughts and actions. He devoted himself to teaching his favourite science, first in the School of Arts, then in the Veterinary College, and in the Extra-academical Medicine School, while he pursued various researches, and was a frequent writer on philosophical subjects. When it was proposed to form an Industrial Museum in the Scottish capital, he was selected as the Director, and to him was entrusted the collection of the specimens and models, a task on which he entered *con amore*, and performed well. In 1855 he was also appointed to the newly formed Regius Professorship of Technology, and he gave courses of lectures illustrated by the collection he was engaged in amassing.

* The obituary notice of Professor Wilson has been kindly communicated by Dr. J. H. Gladstone.

But his labours were interrupted by frequent attacks of illness; his life became every year more precarious; he declined higher honours; and lecturing till within four days of the close of his life, he died on November 22, 1859. His funeral was a public one, attended by multitudes of all classes, his fellow-professors, and pupils, the townspeople who had listened to his popular lectures, the artizans whose affections he had won during his technological inquiries, and a large number of private friends to whom he was endeared by the freshness of his genius, the liveliness and wit of his discourse, the unselfishness and amiability of his character, and the genuineness of his piety.

It was as an expounder of science rather than as a discoverer that Dr. Wilson excelled; yet, exclusive of lectures and larger works, he published about thirty papers on subjects connected with Chemistry, General Physics, or Physiology. Some of these are to be found in our Memoirs or Quarterly Journal, others in the Edinburgh Philosophical Transactions, or elsewhere. Many of these communications have for their object the enforcement and further illustration of the views of other observers, and the inventing of crucial experiments for deciding between rival hypotheses. He boldly commenced with an "Experimental demonstration of the existence of Haloid salts in solution;" he then exploded the reputed conversion of Carbon into Silicon; but his most complete research of a chemical nature was that into the occurrence of Fluorine in the animal, vegetable, and mineral kingdoms, on which he published a series of papers. His researches on colour-blindness belong of course to another branch of science. He was particularly fond of tracing the history of inventions (as that of the air-pump), and he wrote several monographs on eminent chemists, besides his larger work, the "Life of Cavendish." But Professor Wilson's chief strength lay in explaining newly discovered scientific truths, and rendering them attractive by copious illustrations. Hence his popularity as a lecturer, and success as a writer. His little book on Chemistry, in Chambers's Educational Course, has attained a sale of twenty-four thousand; and his treatise on the Electric Telegraph, his "Five gateways of knowledge," and other small publications, have done much to diffuse a taste for experimental philosophy.

The Society then proceeded to the election of the Council and Officers for the ensuing year (for the List, see page 94 of this volume.)

THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY OF LONDON.

Dr.

		£	s.	d.	£	s.	d.
1859. March 26.	To Cash in hand				519	5	4
July	,, Half-Year's Dividend on £450 3 per cent. Consols				6	12	3
1860. March.	,, Ditto ditto ditto				6	7	9
,,	,, Sundry Receipts from 25th March, 1859, to 24th March, 1860, as below—						
	Life Compositions	40	0	0			
	Admission Fees	64	0	0			
	Resident Members' Subscription previous to 1859	10	0	0			
	Non-Resident ditto	16	0	0			
	Resident ditto for 1859	32	0	0			
	Non-Resident ditto ,,	67	0	0			
	Resident ditto for 1860	196	0	0			
	Non-Resident ditto ,,	89	0	0			
	Non-Resident ditto for 1861	1	0	0			
					515	0	0
					£1047	5	4

Cr.

		£	s.	d.	£	s.	d.
1860. March 24.	By Editor's Salary	50	0	0			
	,, ditto Translating	2	5	0			
	,, ditto Honorarium	10	0	0			
					62	5	0
	,, Printing Journal				201	12	4
	,, Librarian's Salary to 1 Jan., 1860				15	0	0
	,, Collector's Commission				25	15	0
	,, Clerk				2	0	0
	,, T. Hux, Cleaning and Attendance, from March, 1859 to March, 1860				20	0	0
	,, Petty Expenses, as per Book				5	4	10
	,, Gate Porter				1	1	0
	,, Royal Society, Share of Tea Expenses				17	17	0
	,, Subscription to Cavendish Society				1	1	0
	,, Books and Magazines				13	7	6
	,, Bookbinding				6	9	6
	,, Stamps, Postage, Envelopes, Stationery, Cab Hire, &c.				8	11	5
	,, Clock (C. Frodsham)				11	0	0
					391	4	7
1859. May 9.	,, Purchase of £100 3 per cent. Consols				90	17	6
					482	2	1
1860. March 24.	,, Balance at Coutts's	515	3	3			
,, ,,	,, Ditto in Cash	50	0	0			
					565	3	3
					£1047	5	4

ASSETS.

	£	s.	d.
Balance in Cash	565	3	3
Invested in 3 per cent Consols	450	0	0
	£1,015	3	3

Examined and found correct, W. H. THORNTHWAITE, W. H. PERKIN, E. A. HADOW, *Auditors.*

April, 5, 1860.

Dr. W. A. Miller, Vice-President, in the Chair.

Dr. Thomas Andrews delivered a discourse on "Ozone."

The following donations have been received:—

"Annales de Chimie" (1789 to 1805), 55 volumes: from Dr. R. D. Thomson.

"Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt," No. 3, für 1859: from the Institute.

"Chemical News," Nos. 13, 14, 15: from the Publishers.

"Journal of the Society of Arts," Nos. 380, 381, 382: from the Society.

"Journal of the Photographic Society" for March, 1860: from the Society.

"Literary Gazette," Nos. 89, 90: from the Publishers.

"On the Composition of the Photographic Image," by John Spiller, Esq.: from the Author.

April 19, 1860.

Robert Warington, Esq., in the Chair.

The following were elected Fellows of the Society:—

M. J. Stark, Esq., Norwich; J. A. R. Newlands, Esq., 19, West-square, Southwark; J. McDonnell, Esq., 71, Great Strand-street, Dublin; C. E. Long, Esq., Westcroft-place, Hammersmith; F. Sutton, Esq., Norwich.

The following papers were read:—

"On the artificial production of Tartaric Acid," by Messrs. Perkin and Duppa.

"On Crystallized Potassium and Sodium," by Mr. C. E. Long.

"On the History of Cinnamic Acid," by Mr. D. Howard.

"On the action of Sodium on Iodide of Methyl," by Messrs. Wanklyn and Buckheisen.

The following donations have been received:—

"Bulletin de l'Académie Impériale des Sciences de St. Pétersbourg," Tome I., Feuilles 1—9: from the Academy.

"American Journal of Science and Arts," March, 1860: from the Editors.

"Canadian Journal," March, 1860: from the Editors.

"Atlantis," No. V.: from the Catholic University of Ireland.

"Two Orations delivered before the Academy of Sciences at Munich:" from the Academy.

"Report of Experiments with different Manures on Permanent Meadow Land," by J. B. Lawes, Esq., F.R.S., and Dr. J. H. Gilbert, F.R.S.: from the Authors.

May 3, 1860.

Professor Brodie, President, in the Chair.

William Proctor, Esq., Petergate, York, was elected a Fellow of the Society.

Dr. J. H. Gladstone delivered a discourse "On Circular Polarization."

The following donations have been received:—

"Transactions of the Royal Society of Edinburgh," Vol. XXII., Part 1.

"Proceedings of the Royal Society of Edinburgh," Session 1858–59: from the Society.

"Pharmaceutical Journal" for May, 1860: from the Editors.

"Chemical News," Nos. 16—21: from the Publishers.

"Journal of the Franklin Institute" for February, 1860: from the Institute.

"Journal of the Photographic Society" for April, 1860: from the Society.

"Literary Gazette," Nos. 91—94: from the Publishers.

"Journal of the Society of Arts," Nos. 383—387: from the Society.

May 17, 1860.

Robert Porrett, Esq., Vice-President, in the Chair.

The following papers were read:—

"On Zinc-methyl," by Mr. J. A. Wanklyn.
"On the Stibethyls and Stibmethyls," by G. B. Buckton.
"On some derivatives from the Olefines," by Dr. Guthrie.

The following donations have been received:—

"Proceedings of the Academy of Natural Sciences of Philadelphia," Nos. 1—5, for 1860: from the Academy.

"Journal of the Society of Arts," No. 388, 389, 390: from the Society.

"Journal of the Franklin Institute" for March and April, 1860: from the Institute.

"Quarterly Journal of the Geological Society," May, 1860: from the Society.

"Address delivered at the Anniversary Meeting of the Geological Society of London," February, 1860, by J. Phillips, Esq.: from the Author.

"Journal of the Photographic Society," May, 1860: from the Society.

"Chemical News," Nos. 22, 23: from the Publishers.

June 7, 1860.

Professor Brodie, President, in the Chair.

Dr. Frankland delivered a discourse on Organo-metallic bodies.

The following donations have been received:—

"Denkschriften der kaiserlichen Akademie der Wissenschaften (mathematisch-naturwissenschaftliche Klasse). Band. XVII."

"Sitzungsberichte der kaiserlichen Akademie der Wissenschaften, No. 10—28."

"Register zu den Banden XXI bis XXX:"

from the Academy.

"Jahresbericht für Meteorolgie und Erdmagnetismus. Band VI für 1854."

"Almanach der kaiserlichen Akademie der Wissenschaften für 1849:"

from the Academy.

"Journal of the Society of Arts, Nos. 391—393:" from the Society.

"Chemical News, Nos. 24—26:" from the Publishers.

"Pharmaceutical Journal for June, 1860:" from the Editor.

"Literary Gazette, Nos. 95—98:" from the Publishers.

"Elements of Chemistry," by William Allen Miller, M.D. Part I, "Chemical Physics:" from the Author.

"Experimental Inquiry into the Composition of some of the Animals fed and slaughtered for Human Food," by J. B. Lawes, Esq., F.R.S., and Dr. J. H. Gilbert, F.R.S.: from the Authors.

"Repertory of Patent Inventions," 13 volumes;

"Newton's London Journal of Arts and Sciences:"

from Messrs. De La Rue.

June 21, 1860.

Thomas Graham, Esq., F.R.S., in the Chair.

The following papers were read:—

"On Baudrimont's Protosulphide of Carbon," by Lyon Playfair, C.B., F.R.S.

"On the composition of Hydrated Acids of Constant Boiling point," by H. E. Roscoe, Ph.D.

"On Acetoxybenzamic Acid, an isomer of Hippuric Acid," by G. C. Foster, Esq.

"On the employment of Saccharate of Lime as a Normal Alkaline Solution in Volumetric Analysis," by F. Maxwell Lyte, Esq.

The following donations have been received:—

"Philosophical Transactions," from Part II for 1854 to Part II for 1859: from the Royal Society.

"Observations made at the Magnetical and Meteorological Observatory at St. Helena," Vol. II.: presented by order of the British Government.

"Monthly Notices of the Royal Astronomical Society," No. 7: from the Society.

"Chemical News," Nos. 27, 28: from the Publishers.

"Twenty-seventh Annual Report of the Royal Cornwall Polytechnic Society:" from the Society.

"Journal of the Society of Arts," Nos. 394, 395: from the Society.

"Literary Gazette," Nos. 99—103: from the Publishers.

"Journal of the Photographic Society," June 1860: from the Society.

"Journal of the Franklin Institute," May, 1860: from the Institute.

"On the Alloys of Copper and Zinc," by F. H. Storer: from the Author.

"Photographs of Fluorescent Substances, showing the small Chemical effect of the Light reflected from them:" from Dr. J. H. Gladstone.

XIX.—*On Organo-metallic Bodies.*

A Discourse delivered to the Members of the Chemical Society of London,

By Dr. E. Frankland, F.R.S.

Although organo-metallic bodies, as a distinct class of organic compounds, are, with one exception, the creation of the last ten years, yet the derivatives of these bodies have been known for a much longer period. From the time that an organic acid was first united with a metallic base, these organic compounds containing metals date their existence. It is true that such compounds containing a metallic constituent have not been regarded from this point of view; but a little consideration will serve to show that they stand in the same relation to organo-metallic bodies in the strict sense of the term, as the ethers, alcohols, acids, and numerous other organic families occupy with regard to the alcohol-radicals from which they are derived. Thus zinc-ethyl yields by oxidation ethylate of zinc:

$$\underbrace{ZnC_4H_5}_{\text{Zinc-ethyl.}} + O_2 = \underbrace{ZnO, C_4H_5O}_{\text{Ethylate of zinc.}}$$

a body which, although unknown until formed by this reaction, has undoubted and well-known analogies in the ethylates of potash and soda.

By suitable processes of oxidation, ethylate of zinc may be converted into acetate of zinc.

$$\underbrace{ZnO, C_4H_5O}_{\text{Ethylate of zinc.}} + O_4 = \underbrace{C_4H_3ZnO_4}_{\text{Acetate of zinc.}} + H_2O_2$$

The ethyl-compounds of potassium and sodium also pass through analogous phases of oxidation.

Again potassium-ethyl and sodium-ethyl, under the influence of carbonic acid, yield the propionates of potash and soda:

$$\underbrace{KC_4H_5}_{\text{Potassium-ethyl.}} + C_2O_4 = \underbrace{C_6H_5KO_4}_{\text{Propionate of potash.}}$$

$$\underbrace{NaC_4H_5}_{\text{Sodium-ethyl.}} + C_2O_4 = \underbrace{C_6H_5NaO_4}_{\text{Propionate of soda.}}$$

The same result may also probably be reached by two distinct stages, viz., first by the conversion of potassium-ethyl and sodium-ethyl into the ethylates of potash and soda:

$$\underbrace{KC_4H_5}_{\text{Potassium-ethyl.}} + O_2 = \underbrace{C_4H_5O, KO}_{\text{Ethylate of potash.}}$$

and secondly by the action of carbonic oxide upon these bodies:

$$\underbrace{C_4H_5KO_2}_{\text{Ethylate of potash.}} + C_2O_2 = \underbrace{C_6H_5KO_4}_{\text{Propionate of potash.}}$$

The second stage of this conversion has not yet been experimentally realized, but Berthelot's ingenious production of formiate of potash from carbonic oxide and hydrate of potash exhibits an homologous reaction.

These examples serve to point out the relations existing between organo-metallic bodies in the usual acceptation of the term, and that far more numerous class of derivatives to which the same name might without impropriety be applied; and it is now only necessary to remark that the present discourse will be confined to the consideration of organo-metallic bodies in the usual and more restricted sense of the term.

Formation of Organo-metallic Bodies.

Organo-metallic bodies admit of being produced by a great variety of processes; but these numerous methods of formation, with very few exceptions, admit of being grouped under four heads.

1. *Formation by union of the organic radical in statu nascenti with the metal.*

Upon this method depends the production of *zinc-ethyl*, the reaction being usually expressed by the following equation:

$$2\underbrace{\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}_{\text{Iodide of ethyl.}} + 4Zn = \underbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\} Zn_2}_{\text{Zinc-ethyl.}} + 2\left.\begin{matrix}Zn\\I\end{matrix}\right\}$$

It is, however, very doubtful whether this equation correctly expresses the actual change which occurs in the production of zinc-ethyl. It has long been known that this body is found in a free state, in very small quantity only, amongst the products of the

reaction of zinc upon iodide of ethyl, but that there exists amongst these products a crystalline body which contains zinc, ethyl, and iodine, and which may be regarded as formed according to the equation:

$$\underbrace{\left.\begin{matrix}C_4H_5\\ I\end{matrix}\right\}}_{\text{Iodide of ethyl.}} + Zn_2 = \underbrace{Zn_2\left\{\begin{matrix}C_4H_5\\ I\end{matrix}\right.}_{\text{Ethiodide of zinc.}}$$

This compound is decomposed at about 150° C, yielding iodide of zinc and zincethyl:

$$\underbrace{2Zn_2\left\{\begin{matrix}C_4H_5\\ I\end{matrix}\right.}_{\text{Ethiodide of zinc.}} = \underbrace{Zn_2\left\{\begin{matrix}C_4H_5\\ C_4H_5\end{matrix}\right.}_{\text{Zincethyl.}} + 2\left.\begin{matrix}Zn\\ I\end{matrix}\right\}$$

Contemporaneously with the first of the above reactions, there occur others in which ethyl, hydride of ethyl, and ethylene are produced. The separation of ethyl in this reaction is doubtless due to the direct action of zinc upon iodide of ethyl:

$$\underbrace{2\left.\begin{matrix}C_4H_5\\ I\end{matrix}\right\}}_{\text{Iodide of ethyl.}} + Zn_2 = \underbrace{\left.\begin{matrix}C_4H_5\\ C_4H_5\end{matrix}\right\}}_{\text{Ethyl.}} + 2\left.\begin{matrix}Zn\\ I\end{matrix}\right\}$$

whilst the appearance of the secondary products, ethylene and hydride of ethyl, results from the action of the ethiodide of zinc upon iodide of ethyl:

$$\underbrace{Zn_2\left\{\begin{matrix}C_4H_5\\ I\end{matrix}\right.}_{\text{Ethiodide of zinc.}} + \underbrace{\left.\begin{matrix}C_4H_5\\ I\end{matrix}\right\}}_{\text{Iodide of ethyl.}} = \underbrace{\left.\begin{matrix}C_4H_5\\ H\end{matrix}\right\}}_{\text{Hydride of ethyl.}} + \underbrace{C_4H_4}_{\text{Ethylene.}} + 2\left.\begin{matrix}Zn\\ I\end{matrix}\right\}$$

a view which is supported by the behaviour of sodium-ethyl in contact with iodide of ethyl.*

$$\underbrace{K_2\left\{\begin{matrix}C_4H_5\\ C_4H_5\end{matrix}\right.}_{\text{Potassium-ethyl.}} + \underbrace{2\left.\begin{matrix}C_4H_5\\ I\end{matrix}\right\}}_{\text{Iodide of ethyl.}} = \underbrace{2\,C_4H_4}_{\text{Ethylene.}} + \underbrace{2\left.\begin{matrix}C_4H_5\\ H\end{matrix}\right\}}_{\text{Hydride of ethyl.}} + 2\,KI$$

Notwithstanding the intermediate stage just indicated in the production of zinc-ethyl, the final result of the reaction is correctly expressed in the first of the above equations.

* Proceedings of Royal Soc., vol. ix, p. 345.

Zinc-methyl and *zinc-amyl* are produced in a perfectly analogous manner, but no attempt has yet been made to form the corresponding compounds of the remaining alcohol-radicals.

The same method of formation yields *cadmium-ethyl,** when iodide of ethyl is digested with cadmium at a temperature of from 100° to 150° C.

$$\underbrace{2\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}_{\text{Iodide of ethyl.}} + Cd_4 = \underbrace{Cd_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Cadmium-ethyl.}} + 2\left.\begin{matrix}Cd\\I\end{matrix}\right\}$$

In this case also there appears to be an intermediate stage in the process, probably quite analogous to that noticed in the production of zinc-ethyl.

The temperature at which the ethiodide of cadmium thus formed is decomposed (177° C.) is considerably higher than that required for the decomposition of the corresponding zinc-compound, in consequence of which a small proportion only of cadmium-ethyl is obtained, the remainder being broken up into other products. This circumstance has hitherto prevented the complete investigation of cadmium-ethyl. The experiments of Wanklyn however scarcely permit its existence to be doubted.

No other organo-cadmium compounds have been formed.

Treated with iodide of ethyl, magnesium gives *magnesium ethyl,*† the reaction commencing briskly at ordinary temperatures, but requiring a heat of 120° C to 130° C for its completion:

$$\underbrace{2\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}_{\text{Iodide of ethyl.}} + Mg_4 = \underbrace{Mg_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Magnesium-ethyl.}} + 2\left.\begin{matrix}Mg\\I\end{matrix}\right\}$$

The homologous reaction with iodide of methyl appears also to yield *magnesium-methyl.*‡

Similarly treated, aluminum yields at temperatures from 100° to 130° C, *aluminium-ethyl* and *aluminium-methyl.*§

$$3\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\} + Al_4 = \left(Al_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right. + Al_2\left\{\begin{matrix}I\\I\\I\end{matrix}\right.\right)$$

$$3\left.\begin{matrix}C_2H_3\\I\end{matrix}\right\} + Al_4 = \left(Al_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right. + Al_2\left\{\begin{matrix}I\\I\\I\end{matrix}\right.\right)$$

* Wanklyn, Chem. Soc. Qu. J.,ix, 193.

† Cahours, Ann. Ch. Phys. [3], lviii, 17. ‡ Ibid, p. 19. § Ibid, p. 20.

Double compounds of aluminium-ethyl and aluminium-methyl with the iodide of aluminium are here formed, and the organo-aluminium bodies have not yet been obtained with certainty free from iodide of aluminium.

*Glucinum-ethyl** appears also to be formed under similar circumstances, but its existence has not yet been confirmed by analysis.

Organo-compounds of Tin.—Although these bodies can be obtained by other processes, the general method we are now considering is doubtless the most convenient mode of producing most of them. Tin is capable of forming three distinct classes of binary inorganic compounds which may be represented by the following general formulæ:

$$Sn_2\left\{\begin{matrix}R\\R\end{matrix}\right. \qquad Sn_2\left\{\begin{matrix}R\\R\\R\end{matrix}\right. \qquad Sn_2\left\{\begin{matrix}R\\R\\R\\R\end{matrix}\right.$$

This threefold atomic character of the metal tin renders the result of its action upon the iodides of the alcohol-radicals considerably less simple than those we have hitherto considered. Without taking into account compounds to which a still more complex constitution has been assigned, the existence of the following series of organo-metallic bodies containing tin has been established:†

1st Series.	2nd Series.	3rd Series.
$Sn_2\left\{\begin{matrix}R+\\R+\end{matrix}\right.$	$Sn_2\left\{\begin{matrix}R+\\R+\\R+\end{matrix}\right.$	$Sn_2\left\{\begin{matrix}R+\\R+\\R-\end{matrix}\right.$
4th Series.	5th Series.	6th Series.
$Sn_2\left\{\begin{matrix}R+\\R+\\R+\\R+\end{matrix}\right.$	$Sn_2\left\{\begin{matrix}R+\\R+\\R+\\R-\end{matrix}\right.$	$Sn_2\left\{\begin{matrix}R+\\R+\\R-\\R-\end{matrix}\right.$

The second and fourth of these series have not yet been produced by the method we are now considering.

* Cahours, Ann. Ch. Phys. [3], lviii, 22.

† In these formulæ R+ represents a positive organic radical, and R— a negative radical: no negative organic radical, as such, has yet been introduced into these compounds.

FIRST SERIES. *Stannous ethide* $\left(Sn_2 \begin{cases} C_4H_5 \\ C_4H_5 \end{cases}\right)$ is produced in small quantities by the action of heat upon a mixture of iodide of ethyl and tin:

$$\underbrace{2\left.\begin{matrix} C_4H_5 \\ I \end{matrix}\right\}}_{\text{Iodide of ethyl.}} + Sn_4 = \underbrace{Sn_2 \begin{cases} C_4H_5 \\ C_4H_5 \end{cases}}_{\text{Stannous ethide.}} + Sn_2 \begin{cases} I \\ I \end{cases}$$

Stannous methide is doubtless formed under similar conditions:

$$\underbrace{2\left.\begin{matrix} C_2H_3 \\ I \end{matrix}\right\}}_{\text{Iodide of methyl.}} + Sn_4 = \underbrace{Sn_2 \begin{cases} C_2H_3 \\ C_2H_3 \end{cases}}_{\text{Stannous methide.}} + Sn_2 \begin{cases} I \\ I \end{cases}$$

The THIRD SERIES of stann-organic compounds are formed by the following reactions:

$$\underbrace{2\left.\begin{matrix} C_2H_3 \\ I \end{matrix}\right\}}_{\text{Iodide of methyl.}} + Sn_3 = \underbrace{Sn_2 \begin{cases} C_2H_3 \\ C_2H_3 \\ I \end{cases}}_{\text{Dimethiodide of tin.}} + SnI$$

$$\underbrace{2\left.\begin{matrix} C_4H_5 \\ I \end{matrix}\right\}}_{\text{Iodide of ethyl.}} + Sn_3 = \underbrace{Sn_2 \begin{cases} C_4H_5 \\ C_4H_5 \\ I \end{cases}}_{\text{Diethiodide of tin.}} + SnI$$

FIFTH SERIES. The following chemical changes express the mode of formation of compounds belonging to this series:

$$\underbrace{3\left.\begin{matrix} C_2H_3 \\ I \end{matrix}\right\}}_{\text{Iodide of methyl.}} + Sn_4 = \underbrace{Sn_2 \begin{cases} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ I \end{cases}}_{\text{Stannic Iodotrimethide.}} + Sn_2 \begin{cases} I \\ I \end{cases}$$

$$\underbrace{3\left.\begin{matrix} C_4H_5 \\ I \end{matrix}\right\}}_{\text{Iodide of ethyl.}} + Sn_4 = \underbrace{Sn_2 \begin{cases} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ I \end{cases}}_{\text{Stannic Iodotriethide.}} + Sn_2 \begin{cases} I \\ I \end{cases}$$

SIXTH SERIES.—The most abundant products of the action of tin upon the iodides of the alcohol-radicals belong to this series; indeed, if the action be produced by light instead of heat, this series of bodies is formed almost to the complete exclusion of the

others. It is necessary, however, to remark that the materials exposed to light should be completely excluded from atmospheric oxygen, otherwise the liquid assumes an orange colour, and the action is so effectually arrested that an exposure for several months to sunlight, concentrated by a parabolic mirror, will scarcely produce any appreciable change. The following reactions explain the formation of bodies belonging to this series:

$$\underbrace{2\left.\begin{matrix}C_2\,H_3\\ I\end{matrix}\right\}}_{\text{Iodide of methyl.}} + Sn_2 = \underbrace{Sn_2\left\{\begin{matrix}C_2\,H_3\\ C_2\,H_3\\ I\\ I\end{matrix}\right.}_{\text{Stannic dimethiodide.}}$$

$$\underbrace{2\left.\begin{matrix}C_4\,H_5\\ I\end{matrix}\right\}}_{\text{Iodide of ethyl.}} + Sn_2 = \underbrace{Sn_2\left\{\begin{matrix}C_4\,H_5\\ C_2\,H_3\\ I\\ I\end{matrix}\right.}_{\text{Stannic diethiodide.}}$$

$$\underbrace{2\left.\begin{matrix}C_{10}H_{11}\\ I\end{matrix}\right\}}_{\text{Iodide of amyl.}} + Sn_2 = \underbrace{Sn_2\left\{\begin{matrix}C_{10}H_{11}\\ C_{10}H_{11}\\ I\\ I\end{matrix}\right.}_{\text{Stannic diamyliodide.}}$$

It is evident that three series of tin-compounds are still wanting to complete the category, viz.:

$$Sn_2\left\{\begin{matrix}R & +\\ R & -\end{matrix}\right. \qquad Sn_2\left\{\begin{matrix}R & +\\ R & -\\ R & -\\ R & -\end{matrix}\right. \qquad Sn_2\left\{\begin{matrix}R & +\\ R & -\\ R & -\end{matrix}\right.$$

It is somewhat remarkable that no organo-tin compounds containing only one equivalent of positive radical, have hitherto been produced. The inference to be drawn from this, that such bodies do not exist, must be checked by the fact that no special attempts have yet been made to form them.

Organo-compounds of Mercury.—The reaction of mercury upon the iodides of the alcohol-radicals gives rise to two series of organic compounds, the general formulæ of which may be thus written:

1st Series.	2nd Series.
$Hg\begin{cases}R\ +\\R\ -\end{cases}$	$Hg\begin{cases}R\ +\\R\ +\end{cases}$

The first series only of these bodies can be produced by the general mode of formation now under consideration; but the members of the second series are readily obtained by the action of an organo-zinc compound upon those of the first.

For the production of the first series of these bodies, the action of light is essential, except in the case of mercuric iodo-allide, no elevation of temperature being capable of producing the chemical change. The following equations sufficiently exhibit the nature of the reaction:

$$\underbrace{\left.\begin{matrix}C_2H_3\\I\end{matrix}\right\}}_{\text{Iodide of methyl.}} + Hg = \underbrace{Hg\begin{cases}C_2H_3\\I\end{cases}}_{\text{Mercuric iodomethide.}}$$

$$\underbrace{\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}_{\text{Iodide of ethyl.}} + Hg = \underbrace{Hg\begin{cases}C_4H_5\\I\end{cases}}_{\text{Mercuric iodoethide.}}$$

$$\underbrace{\left.\begin{matrix}C_6H_5\\I\end{matrix}\right\}}_{\text{Iodide of allyl.}} + Hg = \underbrace{Hg\begin{cases}C_6H_5\\I\end{cases}}_{\text{Mercuric iodo-allide,}}$$

For the production of the methyl-compound, bright sunlight may be employed; but the reaction for the ethyl-body must be conducted in diffused daylight only, otherwise no organo-mètallic compound will be produced, the ethyl being eliminated chiefly as such, but partly, also, as hydride of ethyl and ethylene:

$$\underbrace{2\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}_{\text{Iodide of ethyl.}} + Hg_2 = 2HgI + \underbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}}_{\text{Ethyl.}}$$

$$\underbrace{2\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}_{\text{Iodide of ethyl.}} + Hg_2 = 2HgI + \underbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}_{\text{Hydride of ethyl.}} + \underbrace{C_4H_4}_{\text{Ethylene.}}$$

In addition to these bodies, compounds containing arsenic and antimony can also be produced by this general mode of formation; but they are obtained with greater facility by the second method, which will now be described.

2. *Formation of organo-metallic bodies by the action of the respective metals alloyed with potassium or sodium upon the iodides of the alcohol-radicals.*

The principles involved in this second general mode of production are essentially similar to those in the first, but there is here less tendency to form compounds containing negative as well as positive radicals. This method, although not capable of such general application, is more especially adapted to the formation of the organic compounds of the polyatomic metals. The simultaneous production of an organo-potassium or sodium compound need not be feared, since such compounds cannot exist in the presence of the iodides of the alcohol-radicals.

This mode of formation will be sufficiently illustrated by the following reactions:

Arsenic-compounds.

$$\underbrace{2\left.\begin{array}{r}C_2H_3\\ I\end{array}\right\}}_{\text{Iodide of methyl.}} + As\left\{\begin{array}{l}Na\\ Na\end{array}\right. = \underbrace{As\left\{\begin{array}{l}C_2H_3\\ C_2H_3\end{array}\right.}_{\text{Cacodyl.}} + 2NaI$$

$$\underbrace{2\left.\begin{array}{r}C_4H_5\\ I\end{array}\right\}}_{\text{Iodide of ethyl.}} + As\left\{\begin{array}{l}Na\\ Na\end{array}\right. + \underbrace{As\left\{\begin{array}{l}C_4H_5\\ C_4H_5\end{array}\right.}_{\text{Ethyl-cacodyl.}} + 2NaI$$

$$\underbrace{3\left.\begin{array}{r}C_2H_3\\ I\end{array}\right\}}_{\text{Iodide of methyl.}} + As\left\{\begin{array}{l}Na\\ Na\\ Na\end{array}\right. = \underbrace{As\left\{\begin{array}{l}C_2H_3\\ C_2H_3\\ C_2H_3\end{array}\right.}_{\text{Trimethylarsine.}} + 3NaI$$

$$\underbrace{3\left.\begin{array}{r}C_4H_5\\ I\end{array}\right\}}_{\text{Iodide of ethyl.}} + As\left\{\begin{array}{l}Na\\ Na\\ Na\end{array}\right. = \underbrace{As\left\{\begin{array}{l}C_4H_5\\ C_4H_5\\ C_4H_5\end{array}\right.}_{\text{Triethylarsine.}} + 3NaI$$

$$\underbrace{4\left.\begin{array}{r}C_2H_3\\ I\end{array}\right\}}_{\text{Iodide of methyl.}} + As\left\{\begin{array}{l}Na\\ Na\\ Na\end{array}\right. = \underbrace{As\left\{\begin{array}{l}C_2H_3\\ C_2H_3\\ C_2H_3\\ C_2H_3\\ \quad I\end{array}\right.}_{\text{Iodide of tetra-methylarsonium.}} + 3NaI$$

$$4\left.\begin{matrix}C_4H_5\\ I\end{matrix}\right\} + As\left\{\begin{matrix}Na\\ Na\\ Na\end{matrix}\right. = As\left\{\begin{matrix}C_4H_5\\ C_4H_5\\ C_4H_5\\ C_4H_5\\ I\end{matrix}\right. + 3NaI$$

Iodide of methyl. — Iodide of tetra-ethylarsonium.

Antimony-compounds.

$$3\left.\begin{matrix}C_2H_3\\ I\end{matrix}\right\} + Sb\left\{\begin{matrix}Na\\ Na\\ Na\end{matrix}\right. = Sb\left\{\begin{matrix}C_2H_3\\ C_2H_3\\ C_2H_3\end{matrix}\right. + 3NaI$$

Iodide of methyl. — Trimethylstibine.

$$3\left.\begin{matrix}C_4H_5\\ I\end{matrix}\right\} + Sb\left\{\begin{matrix}Na\\ Na\\ Na\end{matrix}\right. = Sb\left\{\begin{matrix}C_4H_5\\ C_4H_5\\ C_4H_5\end{matrix}\right. + 3NaI$$

Iodide of ethyl. — Triethylstibine.

$$3\left.\begin{matrix}C_{10}H_{11}\\ I\end{matrix}\right\} + Sb\left\{\begin{matrix}Na\\ Na\\ Na\end{matrix}\right. = Sb\left\{\begin{matrix}C_{10}H_{11}\\ C_{10}H_{11}\\ C_{10}H_{11}\end{matrix}\right. + 3NaI$$

Iodide of amyl. — Triamylstibine.

$$4\left.\begin{matrix}C_2H_3\\ I\end{matrix}\right\} + Sb\left\{\begin{matrix}Na\\ Na\\ Na\end{matrix}\right. = Sb\left\{\begin{matrix}C_2H_3\\ C_2H_3\\ C_2H_3\\ C_2H_3\\ I\end{matrix}\right. + 3NaI$$

Iodide of methyl. — Iodide of tetra-methylstibonium.

$$4\left.\begin{matrix}C_4H_5\\ I\end{matrix}\right\} + Sb\left\{\begin{matrix}Na\\ Na\\ Na\end{matrix}\right. = Sb\left\{\begin{matrix}C_4H_5\\ C_4H_5\\ C_4H_5\\ C_4H_5\\ I\end{matrix}\right. + 3NaI$$

Iodide of ethyl. — Iodide of tetre-thylstibonium.

$$4\left.\begin{matrix}C_{10}H_{11}\\ I\end{matrix}\right\} + Sb\left\{\begin{matrix}Na\\ Na\\ Na\end{matrix}\right. = Sb\left\{\begin{matrix}C_{10}H_{11}\\ C_{10}H_{11}\\ C_{10}H_{11}\\ C_{10}H_{11}\\ I\end{matrix}\right. + 3NaI.$$

Iodide of amyl. — Iodide of tetra-mylstibonium.

Tin-compounds.

$$\underbrace{2\left.\begin{matrix} C_2H_3 \\ I \end{matrix}\right\}}_{\text{Iodide of methyl.}} + Sn_2\left\{\begin{matrix} Na \\ Na \end{matrix}\right. = \underbrace{Sn_2\left\{\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right.}_{\text{Stannous-methide.}} + 2NaI$$

$$\underbrace{3\left.\begin{matrix} C_2H_3 \\ I \end{matrix}\right\}}_{\text{Iodide of methyl.}} + Sn_2\left\{\begin{matrix} Na \\ Na \\ Na \end{matrix}\right. = \underbrace{Sn_2\left\{\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_2H_3 \end{matrix}\right.}_{\text{Stann-sesquimethide.}} + 3NaI$$

$$\underbrace{4\left.\begin{matrix} C_2H_3 \\ I \end{matrix}\right\}}_{\text{Iodide of methyl.}} + Sn_2\left\{\begin{matrix} Na \\ Na \\ Na \\ Na \end{matrix}\right. = \underbrace{Sn_2\left\{\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ C_2H_3 \end{matrix}\right.}_{\text{Stannic methide.}} + 4NaI$$

Analogous reactions also represent the formation of the corresponding compounds containing ethyl and amyl.

Lead-compound.

$$\underbrace{3\left.\begin{matrix} C_4H_5 \\ I \end{matrix}\right\}}_{\text{Iodide of ethyl.}} + Pb_2\left\{\begin{matrix} Na \\ Na \\ Na \end{matrix}\right. = \underbrace{Pb_2\left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{matrix}\right.}_{\text{Plumb-sesquiethide.}} + 3NaI$$

Bismuth-compound.

$$\underbrace{3\left.\begin{matrix} C_4H_5 \\ I \end{matrix}\right\}}_{\text{Iodide of ethyl.}} + Bi\left\{\begin{matrix} Na \\ Na \\ Na \end{matrix}\right. = \underbrace{Bi\left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{matrix}\right.}_{\text{Bis-triethide.}} + 3NaI$$

Tellurium-compounds.

Organo-tellurium compounds are formed by a modification of this method, which consists in distilling telluride of potassium with sulphovinate of potash and its homologues.

$$\underbrace{2(C_2H_3O.SO_3 + KO.SO_3)}_{\text{Sulphomethylate of potash.}} + 2KTe = \underbrace{Te_2\left\{\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right.}_{\text{Tellurium-methyl.}} + 4(KO.SO_3)$$

The ethyl and amyl compounds are prepared by homologous reactions.

3. *Formation of organo-metallic bodies by the action of the zinc-compounds of the organic radicals upon the haloid compounds either of the metals themselves or of their organo-derivatives.*

For the production of organo-metallic bodies containing less positive metals than zinc, this method is perhaps not only the most

convenient, but also capable of the most general application. Compounds containing mercury, tin, lead, antimony, and arsenic, have been thus produced, but it has failed when applied to the haloid compounds of copper, silver, and platinum, for although these bodies are violently acted upon, the organic group does not unite with the metals.

The following reactions represent the present state of our knowledge with regard to this method of formation:—

Mercury-compounds.

$$\underbrace{Zn_2 \left\{\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right.}_{\text{Zinc-methyl.}} + Hg \left\{\begin{matrix} Cl \\ Cl \end{matrix}\right. = \underbrace{Hg \left\{\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right.}_{\text{Mercuric methide.}} + 2ZnCl$$

$$\underbrace{Zn_2 \left\{\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right.}_{\text{Zinc-methyl.}} + 2Hg \left\{\begin{matrix} Cl \\ Cl \end{matrix}\right. = \underbrace{2Hg \left\{\begin{matrix} C_2H_3 \\ Cl \end{matrix}\right.}_{\text{Mercuric chloromethide.}} + 2ZnCl$$

$$\underbrace{Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.}_{\text{Zinc-ethyl.}} + Hg \left\{\begin{matrix} Cl \\ Cl \end{matrix}\right. = \underbrace{Hg \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.}_{\text{Mercuric ethide.}} + 2ZnCl$$

$$\underbrace{Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.}_{\text{Zinc-ethyl.}} = 2Hg \left\{\begin{matrix} Cl \\ Cl \end{matrix}\right. = \underbrace{2Hg \left\{\begin{matrix} C_4H_5 \\ Cl \end{matrix}\right.}_{\text{Mercuric chlorethide.}} + 2ZnCl$$

Mercurous ethide and mercurous methide have not yet been obtained either by this or any other process. The instability of mercurous compounds, as seen in the inorganic oxide and iodide, is brought to a climax in organic mercurous compounds; the latter are instantly transformed into metallic mercury and the more stable organo-mercuric compounds. Thus, when zinc-ethyl acts upon mercurous chloride, the following change results:—

$$\underbrace{Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.}_{\text{Zinc-ethyl.}} + 2HgCl = \underbrace{Hg \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.}_{\text{Mercuric ethide.}} + Hg + 2ZnCl$$

Tin-compounds.

$$\underbrace{2Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.}_{\text{Zinc-ethyl.}} + \underbrace{Sn_2 \left\{\begin{matrix} Cl \\ Cl \\ Cl \\ Cl \end{matrix}\right.}_{\text{Stannic chloride.}} = \underbrace{Sn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{matrix}\right.}_{\text{Stannic ethide.}} + 4ZnCl$$

$$\underbrace{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zinc-ethyl.}} + \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\I\\I\end{matrix}\right.}_{\text{Stannic diethiodide.}} = \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Stannic ethide.}} + 2ZnI$$

$$\underbrace{3Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zinc-ethyl.}} + 2Sn_2\left\{\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right. = \underbrace{2Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\Cl\end{matrix}\right.}_{\text{Chlorotriethide of tin.}} + 6ZnCl$$

$$\underbrace{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zinc-ethyl.}} + Sn_2\left\{\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right. = \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\Cl\\Cl\end{matrix}\right.}_{\text{Stannic dichlorethide.}} + 2ZnCl$$

$$\underbrace{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zinc-ethyl.}} + SnCl = \underbrace{\left.\begin{matrix}Zn\\Sn\end{matrix}\right\}\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zincostannous ethide.}} + ZnCl$$

$$\underbrace{Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Zinc-ethyl.}} + \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\I\\I\end{matrix}\right.}_{\text{Stannic di-iodoethide.}} = \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Stannic diethylomethide.}} + 2ZnI$$

$$\underbrace{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zinc-ethyl.}} + \underbrace{Sn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\I\end{matrix}\right.}_{\text{Stannic iodo-trimethide.}} = \underbrace{2Sn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_4H_5\end{matrix}\right.}_{\text{Stannic ethylotrimethide.}} + 2ZnI$$

Lead-compound.

The following is the only reaction which has hitherto been effected by the method which we are now considering :—

$$\underbrace{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zinc-ethyl.}} + 2PbCl = \underbrace{Pb\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Plumbic ethide.}} + Pb + 2ZnCl$$

Antimony-compounds.

$$\underbrace{3Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Zinc-methyl.}} + 2Sb\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right. = \underbrace{2Sb\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Trimethylstibine.}} + 6ZnCl$$

$$3Zn_2 \begin{cases} C_4H_5 \\ C_4H_5 \end{cases} + 2Sb \begin{cases} Cl \\ Cl \\ Cl \end{cases} = 2Sb \begin{cases} C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{cases} + 6ZnCl$$

Zinc-ethyl. Triethylstibine.

Arsenic-compounds.

$$3Zn_2 \begin{cases} C_2H_3 \\ C_2H_3 \end{cases} + 2As \begin{cases} Cl \\ Cl \\ Cl \end{cases} = 2As \begin{cases} C_2H_3 \\ C_2H_3 \\ C_2H_3 \end{cases} + 6ZnCl$$

Zinc-methyl. Trimethylarsine.

$$3Zn_2 \begin{cases} C_4H_5 \\ C_4H_5 \end{cases} + 2As \begin{cases} Cl \\ Cl \\ Cl \end{cases} = 2As \begin{cases} C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{cases} + 6ZnCl$$

Zinc-ethyl. Triethylarsine.

4. *Formation of organo-metallic bodies by the displacement of a metal in an organo-metallic compound by another and more positive metal.*

Wanklyn, to whom we are indebted for this mode of formation, regards this displacement of one metal by another as a case of true electrolytic decomposition. He thinks that in zinc-ethyl, for instance, ethyl is the electro-negative and zinc the electro-positive member: sodium being more electro-positive than zinc, replaces the latter metal, and forms sodium-ethyl. But he supposes that where the original organo-metallic body contains a metal less electro-positive than the hydrocarbon radical, then the latter, and not the metal, would be eliminated by contact with a more positive metal. Cacodyl, for instance, when treated with sodium should give methyl and arsenide of sodium:

$$As \begin{cases} C_2H_3 \\ C_2H_3 \end{cases} + Na_2 = As \begin{cases} Na \\ Na \end{cases} + \begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\Big\}$$

Cacodyl. Arsenide of sodium. Methyl.

This view, the correctness of which is more than probable, is supported by the action of potassium and of zinc-ethyl upon ammonia:

$$2N \begin{cases} H \\ H \\ H \end{cases} + K_2 = 2N \begin{cases} K \\ H \\ H \end{cases} + H_2$$

Ammonia. Potassamide.

$$\underbrace{2N\begin{cases}H\\H\\H\end{cases}}_{\text{Ammonia.}} + \underbrace{Zn_2\begin{cases}C_4H_5\\C_4H_5\end{cases}}_{\text{Zincethyl.}} = \underbrace{2N\begin{cases}Zn\\H\\H\end{cases}}_{\text{Zincamide.}} + \underbrace{2\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}_{\text{Hydride of ethyl.}}$$

In accordance with this hypothesis, Wanklyn considers that the ethyl in sodium-ethyl would be displaced by copper, mercury, platinum, &c., and that sodium-ethyl is only in equilibrium with bodies, whose respective positions in the electrical scale are either both of them within, or both of them without, the space lying between the electro-positive sodium and the electro-negative ethyl.

This fourth mode of producing organo-metallic bodies has hitherto been applied only to the formation of sodium and potassium compounds, or rather double compounds of these bodies with zincethyl, according to the following reactions:

$$\underbrace{3Zn_2\begin{cases}C_4H_5\\C_4H_5\end{cases}}_{\text{Zincethyl.}} + Na_2 = \underbrace{\left(2Zn_2\begin{cases}C_4H_5\\C_4H_5\end{cases} + Na_2\begin{cases}C_4H_5\\C_4H_5\end{cases}\right)}_{\text{Double compound of sodium-ethyl and zinc-ethyl.}} + Zn_2$$

$$\underbrace{3Zn_2\begin{cases}C_4H_5\\C_4H_5\end{cases}}_{\text{Zincethyl.}} + K_2 = \underbrace{\left(2Zn_2\begin{cases}C_4H_5\\C_4H_5\end{cases} + K_2\begin{cases}C_4H_5\\C_4H_5\end{cases}\right)}_{\text{Double compound of potassium-ethyl and zinc-ethyl.}} + Zn_2$$

Sodium also displaces mercury from mercuric ethide: sodium-ethyl seems to be formed, but the exact nature of the reaction has not been ascertained.

Properties of Organo-metallic Bodies.

The organo-metallic compounds as a class are distinguished for the extraordinary energy of their affinities. With certain exceptions, presently to be noticed, their disposition to unite with negative elements increases with the positive character of the metal and with the smallness of the atomic weight of the alcohol-radical. Thus organo-potassium and sodium compounds possess more chemical energy than those of zinc, whilst the latter are more active than the compounds of arsenic, antimony, tin, or lead. Again, in the series belonging to each metal, the methylic compounds are more energetic than the ethylic ones, whilst the last greatly surpass the amylic compounds in this respect. But whilst

these general principles govern the chemical energy of organo-metallic bodies, their effect appears to be modified by the degree of saturation in which the metal exists. Although this circumstance has hitherto received only very partial elucidation, yet we have evidence of its existence in the case of organo-tin compounds. Both stannous ethide and stannous methide combine directly with atmospheric oxygen, and the union takes place with tolerable rapidity; but neither stannic ethide nor stannic methide is in the least degree acted upon by free oxygen at ordinary temperatures; even iodine acts upon them with difficulty. This diminution of chemical energy in organo-stannic compounds cannot be ascribed to the mere influence of the additional weight of hydrocarbon which they contain, since stannous amylide readily unites with free oxygen at ordinary temperatures, although the single molecule of amyl which it contains is considerably heavier than the double atom of either methyl or ethyl present in the organo-stannic compounds just cited.

Organo-metallic compounds in a state of partial saturation play the part of compound radicals. They are uniatomic, biatomic, teratomic, or quadratomic, according to the number of molecules requisite to complete their saturation. On the other hand, organo-metallic bodies in a state of saturation never perform radical functions, they never undergo chemical change without decomposition. Thus zinc-ethyl, stannic ethide, mercuric ethide, and plumbic ethide all give substitution-products when they are chemically acted upon.

The description of the special properties of the organo-metallic bodies may be conveniently commenced with the most positive of the class, viz.:

*Potassium and sodium series.**—These bodies have not yet been isolated; they are known only in combination with the corresponding zinc-compounds. The double compound of sodium-ethyl and zinc-ethyl is the only one which has hitherto been submitted to analysis. Its formula is

$$2Zn_2 \begin{cases} C_4H_5 \\ C_4H_5 \end{cases} + Na_2 \begin{cases} C_4H_5 \\ C_4H_5 \end{cases}$$

This compound first separates from its solution in zinc-ethyl as a transparent fluid, which after some time solidifies to a mass of large tabular crystals, fusing at 27° C., but when once fused

* Wanklyn, Proceedings of Roy. Soc., ix, 341.

remaining fluid at several degrees below that point. On the application of a moderate heat, gases are evolved, and a mixture of sodium and zinc without carbon is left behind. The double compound decomposes water with great violence, forming hydride of ethyl, and the hydrated oxides of zinc and sodium. The behaviour with negative elements has not yet been studied. Its most interesting reaction consists in the absorption of carbonic acid, which it transforms into propionic acid. The sodium-ethyl alone takes part in this reaction :*

$$\underbrace{Na_2 \left\{ \begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix} \right.}_{\text{Sodium-ethyl.}} + 2C_2O_4 = \underbrace{2 \left. \begin{matrix} C_6H_5O_2 \\ Na \end{matrix} \right\} O_2}_{\text{Propionate of soda.}}$$

A similar double compound containing *sodium-methyl*, as well as the potassium-compounds of ethyl and methyl, have been formed. They have not yet been completely investigated, but it is believed that their composition and properties are perfectly analogous to those of sodium-ethyl.

No compound of any of these bodies with a negative element has been obtained. Their action upon carbonic acid proves that they possess a still higher reducing power than the corresponding organo-zinc compounds, and they will therefore doubtless prove valuable agents for the substitution of positive groups for negative elements in cases where organo-zinc compounds fail to produce the desired effect.

Sodium-ethyl decomposes the iodides of the alcohol-radicals in the cold, with formation of iodide of sodium.†

$$\underbrace{Na_2 \left\{ \begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix} \right.}_{\text{Sodium-ethyl.}} + \underbrace{2 \left. \begin{matrix} C_4H_5 \\ I \end{matrix} \right\}}_{\text{Iodide of ethyl.}} = 2NaI + \underbrace{2 \left. \begin{matrix} C_4H_5 \\ H \end{matrix} \right\}}_{\text{Hydride of ethyl.}} + \underbrace{2\,C_4H_4}_{\text{Ethylene.}}$$

Owing to this behaviour, potassium and sodium compounds can only be prepared by method No. 4.

Magnesium series.‡—The compounds containing ethyl and methyl only have hitherto been examined, and the former alone submitted to analysis. These bodies possess a close similarity to

* Wanklyn. Chem. Soc. Qu. J., xi. 103.
† Frankland. Proceedings of Roy. Soc., ix. 345.
‡ Cahours. Ann. Ch. Phys., lviii. 17.

organo-zinc compounds. They are very volatile colourless liquids, possessing a powerful alliaceous odour; are spontaneously inflammable, and decompose water with violence. They do not readily decompose the iodides of the alcohol-radicals, and can therefore be prepared by method No. 1. No compound of these bodies with negative elements has yet been produced. They are in the condition of chemical saturation. Further details of their properties are wanting.

*Aluminium and Glucinum series.**—Like the organo-compounds of the alkaline metals, the aluminium and glucinum compounds have not yet been isolated with certainty; they are known only in combination with the iodides of the respective metals, and the composition of the ethyl and aluminium body only has been fixed by analysis. Its formula is

$$Al_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right. + Al_2\left\{\begin{matrix}I\\I\\I\end{matrix}\right.$$

These double compounds possess great chemical energy; they are spontaneously inflammable, volatile liquids, which decompose water with explosive violence. They are attacked by zinc-ethyl, forming iodide of zinc and very inflammable liquids, which latter are believed to be the pure organo-compounds. They appear to be chemically saturated bodies, and therefore incapable of direct combination. Further details are wanting.

Zinc series.†—Three bodies belonging to this series are known, viz.:

Zinc-methyl	$Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.$
Zinc-ethyl	$Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.$
Zinc-amyl	$Zn_2\left\{\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\end{matrix}\right.$

They are colourless, transparent, mobile, volatile, and odorous liquids, composed of four gaseous volumes of the hydro-carbon

* Cahours, Ann. Ch. Phys., lviii, 20.

† Frankland, Chem. Soc. Qu. J., ii, 297, and iii, 44; Phil. Trans., cxlii, 431, and cxlv, 259. Wanklyn, Chem. Soc. Qu. J., xiii, 124.

radical, and two volumes of zinc-vapour, the six volumes condensed to four. The methyl and ethyl compounds are spontaneously inflammable, burning with a greenish blue flame. All three are saturated compounds incapable of direct combination. In contact with water, they are instantly decomposed, with formation of oxide of zinc and hydride of the organic radical.

$$\underset{\text{Zinc-methyl.}}{\underline{Zn_2 \left\{\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right.}} + \left.\begin{matrix} H \\ H \end{matrix}\right\} O_2 = \left.\begin{matrix} Zn \\ Zn \end{matrix}\right\} O_2 + \underset{\text{Hydride of methyl.}}{\underline{2 \left.\begin{matrix} C_2H_3 \\ H \end{matrix}\right\}}}$$

$$\underset{\text{Zinc-ethyl.}}{\underline{Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.}} + \left.\begin{matrix} H \\ H \end{matrix}\right\} O_2 = \left.\begin{matrix} Zn \\ Zn \end{matrix}\right\} O_2 + \underset{\text{Hydride of ethyl.}}{\underline{2 \left.\begin{matrix} C_4H_5 \\ H \end{matrix}\right\}}}$$

$$\underset{\text{Zinc-amyl.}}{\underline{Zn_2 \left\{\begin{matrix} C_{10}H_{11} \\ C_{10}H_{11} \end{matrix}\right.}} + \left.\begin{matrix} H \\ H \end{matrix}\right\} O_2 = \left.\begin{matrix} Zn \\ Zn \end{matrix}\right\} O_2 + \underset{\text{Hydride of amyl.}}{\underline{2 \left.\begin{matrix} C_{10}H_{11} \\ H \end{matrix}\right\}}}$$

Gradually treated with oxygen, so as to avoid too violent action, they form the respective zinc-alcohols.

$$\underset{\text{Zinc-methyl}}{\underline{Zn_2 \left\{\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right.}} + O_4 = \underset{\text{Methylate of zinc.}}{\underline{2 \left.\begin{matrix} C_2H_3 \\ Zn \end{matrix}\right\} O_2}}$$

$$\underset{\text{Zinc-ethyl.}}{\underline{Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.}} + O_4 = \underset{\text{Ethylate of zinc.}}{\underline{2 \left.\begin{matrix} C_4H_5 \\ Zn \end{matrix}\right\} O_2}}$$

$$\underset{\text{Zinc-amyl.}}{\underline{Zn_2 \left\{\begin{matrix} C_{10}H_{11} \\ C_{10}H_{11} \end{matrix}\right.}} + O_4 = \underset{\text{Amylate of zinc.}}{\underline{2 \left.\begin{matrix} C_{10}H_{11} \\ Zn \end{matrix}\right\} O_2}}$$

The action of iodine upon organo-zinc-compounds consists in the transformation of both their constituents into iodides.

$$\underset{\text{Zinc-methyl.}}{\underline{Zn_2 \left\{\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right.}} + I_4 = 2ZnI + \underset{\text{Iodide of methyl.}}{\underline{2 \left.\begin{matrix} C_2H_3 \\ I \end{matrix}\right\}}}$$

$$\underbrace{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zinc ethyl.}} + I_4 = 2ZnI + \underbrace{2\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}_{\text{Iodide of ethyl.}}$$

$$\underbrace{Zn_2\left\{\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\end{matrix}\right.}_{\text{Zinc-amyl.}} + I_4 = 2ZnI + \underbrace{2\left.\begin{matrix}C_{10}H_{11}\\I\end{matrix}\right\}}_{\text{Iodide of amyl.}}$$

Organo-zinc compounds behave in a manner exactly analogous in contact with the other halogens.

Reactions like the foregoing, point to the applicability of these compounds for effecting the substitution of positive groups for negative elements in compound bodies, an application which has not failed to attract the notice of chemists. In addition to the reactions of this class given above as examples of the formation of organo-metallic bodies by the third method, the following have been realized :

With Binoxide of Nitrogen.*

$$\underbrace{2(N_2O_4)}_{\text{Binoxide of nitrogen.}} + \underbrace{Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Zinc-methyl.}} = \underbrace{2\left.\begin{matrix}N_2C_2H_3O_2\\Zn\end{matrix}\right\}O_2}_{\text{Dinitro-methylate of zinc.}}$$

$$2(N_2O_4) + \underbrace{Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Zinc-ethyl.}} = \underbrace{2\left.\begin{matrix}N_2C_4H_5O_2\\Zn\end{matrix}\right\}O_2}_{\text{Dinitro-ethylate of zinc.}}$$

It will be perceived that these reactions are the exact analogues of the one already mentioned in the sodium and potassium series, where carbonic acid, treated with sodium-methyl and sodium-ethyl, forms acetic and propionic acids. In fact, dinitro-methylic and dinitro-ethylic acids may be regarded as the analogues of acetic and propionic acid respectively; the nitrogen here sustaining a biatomic character, and replacing an equivalent amount of carbon.

With Sulphurous Acid.†

$$\underbrace{2(S_2O_4)}_{\text{Sulphurous acid.}} + \underbrace{Zn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Zinc-methyl.}} + \underbrace{2\left.\begin{matrix}S_2C_2H_3O_2\\Zn\end{matrix}\right\}O_2}_{\text{Methylodithionate of zinc.}}$$

* Frankland, Phil. Trans., 1857, p. 59.

† Hobson, Chem. Soc. Qu. J., x, 55 and 243.

$$3(S_2O_4) + \underbrace{Zn_2 \begin{Bmatrix} C_4H_5 \\ C_4H_5 \end{Bmatrix}}_{\text{Zinc ethyl.}} = \underbrace{2 \left.\begin{matrix} S_3C_4H_5O_4 \\ Zn \end{matrix}\right\} O_2}_{\text{Ethylodithionate of zinc.}}$$

With Terchloride of Phosphorus.*

$$2(PCl_3) + \underbrace{3Zn_2 \begin{Bmatrix} C_2H_3 \\ C_2H_3 \end{Bmatrix}}_{\text{Zinc-methyl.}} = \underbrace{2P \begin{Bmatrix} C_2H_3 \\ C_2H_3 \\ C_2H_3 \end{Bmatrix}}_{\text{Trimethylphosphine.}} + 6ZnCl$$

$$2(PCl_3) + \underbrace{3Zn_2 \begin{Bmatrix} C_4H_5 \\ C_4H_5 \end{Bmatrix}}_{\text{Zinc-ethyl.}} = \underbrace{2P \begin{Bmatrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{Bmatrix}}_{\text{Triethylphosphine.}} + 6ZnCl$$

There is no apparent obstacle to this reaction being pushed to its extreme limit in the case of pentatomic bodies, such as phosphorus, arsenic, or antimony. Mr. Buckton has recently attempted this in the case of antimony; but although evidence of the existence of a pentethide of antimony was obtained, the body could not be isolated and its composition satisfactorily fixed. The great stability of the triatomic compounds of these bodies will probably present considerable difficulty in the way of obtaining pentatomic compounds of an exclusively positive character, such bodies being doubtless easily resolved into the more stable groupings represented in the following equation:

$$\underbrace{Sb \begin{Bmatrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{Bmatrix}}_{\text{Antimonic ethide.}} = \underbrace{Sb \begin{Bmatrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{Bmatrix}}_{\text{Triethylstibine.}} + \underbrace{\left.\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right\}}_{\text{Ethyl.}}$$

Whilst on the one hand, organo-zinc compounds are thus capable of effecting the substitution of their positive organic group for negative elements, they can, on the other hand, in certain cases replace hydrogen by zinc, forming, for instance, with ammonia and its homologues, a series of zincamides. In this direction the following reactions have been recorded.†

* Hofmann and Cahours, Phil. Trans. for 1857, p. 578.
† Frankland, Proc. of Royal Soc., viii, 502.

$$\underset{\text{Zinc-ethyl.}}{Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.} + \underset{\text{Ammonia.}}{2N \left\{\begin{matrix} H \\ H \\ H \end{matrix}\right.} = \underset{\text{Zincamide.}}{2N \left\{\begin{matrix} Zn \\ H \\ H \end{matrix}\right.} + \underset{\text{Hydride of ethyl.}}{2 \left.\begin{matrix} C_4H_5 \\ H \end{matrix}\right\}}$$

$$\underset{\text{Zinc ethyl.}}{Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.} + \underset{\text{Aniline.}}{2N \left\{\begin{matrix} C_{12}H_5 \\ H \\ H \end{matrix}\right.} = \underset{\text{Zincphenylimide.}}{2N \left\{\begin{matrix} C_{12}H_5 \\ Zn \\ H \end{matrix}\right.} + \underset{\text{Hydride of ethyl.}}{2 \left.\begin{matrix} C_4H_5 \\ H \end{matrix}\right\}}$$

$$\underset{\text{Zinc-ethyl.}}{Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.} + \underset{\text{Diethylamine.}}{2N \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ H \end{matrix}\right.} = \underset{\text{Diethyl-zincamide.}}{2N \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ Zn \end{matrix}\right.} + \underset{\text{Hydride of ethyl.}}{2 \left.\begin{matrix} C_4H_5 \\ H \end{matrix}\right\}}$$

$$\underset{\text{Zinc-ethyl.}}{Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.} + \underset{\text{Oxamide.}}{N_2 \left\{\begin{matrix} C_4O_4'' \\ H_2 \\ H_2 \end{matrix}\right.} = \underset{\text{Zincoximide.}}{N_2 \left\{\begin{matrix} C_4O_4'' \\ Zn_2 \\ H_2 \end{matrix}\right.} + \underset{\text{Hydride of ethyl.}}{2 \left.\begin{matrix} C_4H_5 \\ H \end{matrix}\right\}}$$

$$\underset{\text{Zinc-ethyl.}}{Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.} + \underset{\text{Acetamide.}}{2N \left\{\begin{matrix} C_4H_3O_2 \\ H \\ H \end{matrix}\right.} = \underset{\text{Zinc-acetimide.}}{2N \left\{\begin{matrix} C_4H_3O_2 \\ Zn \\ H \end{matrix}\right.} + \underset{\text{Hydride of ethyl.}}{2 \left.\begin{matrix} C_4H_5 \\ H \end{matrix}\right\}}$$

Of the same nature apparently is the reaction between zinc-ethyl and acetic anhydride.*

$$Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right. + \left.\begin{matrix} C_4H_3O_2 \\ C_4H_3O_2 \end{matrix}\right\} O_2 = \left.\begin{matrix} C_4H_2ZnO_2 \\ C_4H_2ZnO_2 \end{matrix}\right\} O_2? + 2 \left.\begin{matrix} C_4H_5 \\ H \end{matrix}\right\}$$

The members of the zinc-series unite with neutral salts to form compounds which have been but little examined. The following, however, are known :†

Dinitromethylate of zinc and zinc-methyl	$2 \left.\begin{matrix} N_2C_2H_3O_2 \\ Zn \end{matrix}\right\} O_2 + Zn_2 \left\{\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right.$
Dinitroethylate of zinc and zinc-ethyl	$2 \left.\begin{matrix} N_2C_4H_5O_2 \\ Zn \end{matrix}\right\} O_2 + Zn_2 \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right.$

* When zinc-ethyl is added to acetic anhydride, torrents of pure hydride of ethyl are evolved; the other product of the reaction has not been examined.

† Frankland, Phil. Trans., 1857, p. 59.

Finally, it has been observed, that zinc-methyl when generated in contact with methylic or vinic ether, combines with these bodies, forming*

Methylate of zinc-methyl $2\left(Zn_2 \begin{cases} C_2H_3 \\ C_2H_3 \end{cases}\right) + \begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\Big\} O_2$

Ethylate of zinc-methyl $2\left(Zn_2 \begin{cases} C_2H_3 \\ C_2H_3 \end{cases}\right) + \begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\Big\} O_2$

Cadmium Series.†—Only one member of this series is known, and that very imperfectly. So far as its properties are made out, they appear to be perfectly analogous to those of the zinc compounds.

Tin Series.‡—A large number of organo-metallic bodies containing tin have been described. The existence of the following may be considered as clearly established.

a. Stannous compounds.

Stannous methide, or stanmethyl $Sn_2 \begin{cases} C_2H_3 \\ C_2H_3 \end{cases}$

Stannous ethide or stanethyl $Sn_2 \begin{cases} C_4H_5 \\ C_4H_5 \end{cases}$

b. Sesqui-compounds.

Sesquimethide of tin $Sn_2 \begin{cases} C_2H_3 \\ C_2H_3 \\ C_2H_3 \end{cases}$

Sesquiethide of tin $Sn_2 \begin{cases} C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{cases}$

Dimethiodide of tin $Sn_2 \begin{cases} C_2H_3 \\ C_2H_3 \\ I \end{cases}$

Diethiodide of tin $Sn_2 \begin{cases} C_4H_5 \\ C_4H_5 \\ I \end{cases}$

* Frankland, Phil. Trans., 1859, p. 412.

† Wanklyn, Chem. Soc. Qu. J., ix, 193.

‡ Frankland, Phil. Trans., 1852, p. 417, and Phil. Trans., 1859, p. 401. Cahours et Riche, Compt. rend., xxxv, 91, and xxxvi, 1001. Löwig, Ann. Ch. Pharm. lxxxiv, 308. A. Grimm, Ann. Ch. Pharm, xcii, 383, Buckton, Phil. Trans. for 1859, p. 423. Cahours, Ann. Ch. Phys., lviii, 22.

c. Stannic compounds.

Stannic methide	$Sn_2 \begin{cases} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ C_2H_3 \end{cases}$
Stannic ethide	$Sn_2 \begin{cases} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{cases}$
Stannic ethylomethide	$Sn_2 \begin{cases} C_2H_3 \\ C_2H_3 \\ C_4H_5 \\ C_4H_5 \end{cases}$
Stannic-ethylo-trimethide	$Sn_2 \begin{cases} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ C_4H_5 \end{cases}$
Stannic iodo-trimethide	$Sn_2 \begin{cases} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ I \end{cases}$
Stannic iodo-triethide	$Sn_2 \begin{cases} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ I \end{cases}$
Stannic iodo-dimethide	$Sn_2 \begin{cases} C_2H_3 \\ C_2H_3 \\ I \\ I \end{cases}$
Stannic iodo-diethide	$Sn_2 \begin{cases} C_4H_5 \\ C_4H_5 \\ I \\ I \end{cases}$

It is scarcely necessary to observe that the iodine in the above compounds admits of replacement by any salt-forming radical and also by oxygen or sulphur.

Stannous compounds are oily liquids soluble in alcohol and ether, but insoluble in water, and possessing a pungent odour. They cannot be distilled without decomposition, being resolved

into stannic compounds and metallic tin. They are in a state of partial chemical saturation only, and therefore perform the part of radicals, combining directly with chlorine, oxygen, &c., and forming well-marked bodies of great stability.

Stannous compounds are biatomic, and unite directly with free oxygen, chlorine, &c., to produce bodies of the stannic form. Thus stannous ethide forms with oxygen, stannic oxydiethide.

$$\underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Stannous ethide.}} \quad + \quad O_2 \quad = \quad \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\O\\O\end{matrix}\right.}_{\text{Stannic oxydiethide.}}$$

Stannous compounds have never yet been observed to play a uniatomic part. No sesqui-compound has been directly formed from a stannous body; the latter, under the influence of iodine, oxygen, &c., seems to pass at once into the stannic form. It must be remarked, however, that no direct experiments have been made with a view of revealing any uniatomic attribute which may attach to stannous compounds.

Sesqui-compounds of the form $Sn_2\left\{\begin{matrix}R+\\R+\\R+\end{matrix}\right.$ have hitherto been very little examined. They are oily liquids, uniting directly with negative radicals, forming an extensive series of compounds belonging to the stannic class, a considerable number of which have been studied. The following examples will serve to show the mode in which sesqui-compounds of this form pass into bodies of the stannic class:

$$\underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Sesquiethide of tin.}} \quad + \quad I \quad = \quad \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\I\end{matrix}\right.}_{\text{Stannic iodotriethide.}}$$

$$\underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\I\end{matrix}\right.}_{\text{Stannic iodotriethide.}} \quad + \quad I_2 \quad = \quad \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\I\\I\end{matrix}\right.}_{\text{Stannic iododiethide.}} \quad + \quad \underbrace{\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}_{\text{Iodide of ethyl.}}$$

No reduction of a sesqui-compound to a stannous compound has yet been effected, although it can scarcely be doubted that an aqueous solution of diethiodide of tin, for instance, if treated with zinc, would yield stannous ethide. On the other hand, stannic ethide or methide in contact with iodine is transformed into a sesqui-compound, viz., diethiodide of tin:

$$\underset{\text{Stannic ethylo-dimethide.}}{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_2H_3\\C_2H_3\end{matrix}\right.} + I_3 = \underset{\text{Diethiodide of tin.}}{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\I\end{matrix}\right.} + \underset{\text{Iodide of methyl.}}{2\left.\begin{matrix}C_2H_3\\I\end{matrix}\right\}}$$

Sesqui-compounds of the form $Sn_2\left\{\begin{matrix}R+\\R+\\R-\end{matrix}\right.$ are very little known. In fact the diethiodide of tin, the production of which from stannic ethylodimethide has just been mentioned, is the only one known with certainty. It is a colourless mobile liquid, boiling with partial decomposition at 208° C., and possessing a most insupportable odour, resembling essential oil of mustard. Heated with excess of iodine, it is transformed into stannic iododiethide:

$$\underset{\text{Diethiodide of tin.}}{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\I\end{matrix}\right.} + I = \underset{\text{Stannic iododiethide.}}{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\I\\I\end{matrix}\right.}$$

Stannic compounds of the form $Sn_2\left\{\begin{matrix}R+\\R+\\R+\\R+\end{matrix}\right.$ are colourless mobile liquids, possessing a slight ethereal odour. They are volatile without decomposition, and are very stable. Being in the condition of chemical saturation, they are incapable of direct combination. No body can act upon them without expelling one or more equivalents of positive radical. Thus, when heated with hydrochloric acid, stannic ethide yields stannic chlorotriethide and hydride of ethyl:

$$\underset{\text{Stannic ethide.}}{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.} + HCl = \underset{\text{Stannic chlorotriethide.}}{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\Cl\end{matrix}\right.} + \underset{\text{Hydride of ethyl.}}{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}$$

With two equivalents of iodine, the reaction is :

$$\underbrace{Sn_2\begin{cases}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{cases}}_{\text{Stannic ethide.}} + I_2 = \underbrace{Sn_2\begin{cases}C_4H_5\\C_4H_5\\C_4H_5\\I\end{cases}}_{\text{Stannic iodotriethide.}} + \underbrace{\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}_{\text{Iodide of ethyl.}}$$

And with four equivalents of iodine :

$$\underbrace{Sn_2\begin{cases}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{cases}}_{\text{Stannic ethide.}} + I_4 = \underbrace{Sn_2\begin{cases}C_4H_5\\C_4H_5\\I\\I\end{cases}}_{\text{Stannic iododiethide.}} + \underbrace{2\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}_{\text{Iodide of ethyl.}}$$

Stannic compounds of the form $Sn_2\begin{cases}R +\\R +\\R +\\R -\end{cases}$, commonly called compounds of sesquistanethyl, have been comparatively well studied. The oxides are, in the anhydrous condition, volatile, limpid, oily liquids which readily unite with water, forming crystalline hydrates which have a powerful alkaline reaction, and neutralize the strongest acids, forming an extensive series of salts. These salts are almost all soluble in water, readily crystallizable, and of a very pungent odour. The stannic iodotriethide and the stannic triethylosulphate may be adduced as examples of the haloïd and oxysalts respectively :

Stannic iodotriethide $Sn_2\begin{cases}C_4H_5\\C_4H_5\\C_4H_5\\I\end{cases}$

Stannic triethylosulphate $Sn_2\begin{cases}C_4H_5\\C_4H_5\\C_4H_5\\SO_4\end{cases}$

Stannic compounds of the form $Sn_2\begin{cases}R +\\R +\\R -\\R -\end{cases}$ have also been very completely investigated. The oxides are white amorphous powders, insoluble in water, alcohol, and ether. They dissolve in hydrochloric, hydriodic, and hydrobromic acids, forming colourless and

inodorous salts, which crystallize in fine prisms. Most of the oxysalts can also be obtained in the crystalline form, either from aqueous or alcoholic solutions. The iodide and sulphate of stannic diethide, which may be regarded as representatives of the haloïd and oxysalts, have the following formulæ:

Stannic ethylodisulphate $Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\SO_4\\SO_4\end{matrix}\right.$

Stannic iododiethide $Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\I\\I\end{matrix}\right.$

Stannic compounds of this form are readily reduced to stannous compounds; thus, when a piece of zinc is plunged into a solution of stannic chlorodiethide, stannous ethide is produced:

$$\underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\Cl\\Cl\end{matrix}\right.}_{\text{Stannic chlorodiethide.}} + Zn_2 = \underbrace{Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Stannous ethide.}} + 2ZnCl$$

BISMUTH SERIES.*—The following bodies belonging to this series have been described:

1. Bismuthous ethide $Bi\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.$

2. Bismuthous dichlorethide $Bi\left\{\begin{matrix}C_4H_5\\Cl\\Cl\end{matrix}\right.$

3. Bismuthous di-iodoethide $Bi\left\{\begin{matrix}C_4H_5\\I\\I\end{matrix}\right.$

4. Bismuthous dioxyethide $Bi\left\{\begin{matrix}C_4H_4\\O\\O\end{matrix}\right.$?

* Breed, Ann. Ch. Pharm., lxxxii, 106; Dünhaupt, Ann. Ch. Pharm., xcii, 371.

5. Double compound of bismuthous sulphide with bismuthic sulphotriethide $\left.\right\}$ $Bi\begin{cases}C_4H_5\\C_4H_5\\C_4H_5\\S\\S\end{cases} + 2Bi\begin{cases}S\\S?\\S\end{cases}$

These bodies have as yet been but very imperfectly investigated. Bismuthous triethide is a colourless or slightly yellow mobile liquid, having an unpleasant odour like that of stibethine. Exposed to the air, it gives off dense yellow fumes, inflames spontaneously, and finally explodes. It is very instable, begins to decompose at 50° or 60° C., and explodes violently when heated to 150° C., a temperature still below its boiling point. No direct compound of this body has yet been obtained; it behaves like a chemically saturated substance, and when slowly oxidized in contact with water, yields alcohol and hydrated oxide of bismuth:

$$\underbrace{Bi\begin{cases}C_4H_5\\C_4H_5\\C_4H_5\end{cases}}_{\text{Bismuthous ethide.}} + 3\left.\begin{matrix}H\\H\end{matrix}\right\}O_2 + O_6 = BiO_3,3HO + 3\underbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}_{\text{Alcohol.}}$$

When an alcoholic solution of bichloride of mercury is added to an alcoholic solution of bismuthous ethide, mercuric ethochloride crystallizes out, whilst bismuthous dichlorethide remains in solution:

$$\underbrace{Bi\begin{cases}C_4H_5\\C_4H_5\\C_4H_5\end{cases}}_{\text{Bismuthous ethide.}} + 2HgCl_2 = \underbrace{Bi\begin{cases}C_4H_5\\Cl\\Cl\end{cases}}_{\text{Bismuthous dichlorethide.}} + \underbrace{2Hg\begin{cases}C_4H_5\\Cl\end{cases}}_{\text{Mercuric chlorethide.}}$$

From the bismuthous dichlorethide, the diiodide and dioxyethide are prepared by double decomposition, whilst the simultaneous action of sulphuretted hydrogen, water, bismuthous ethide, and atmospheric oxygen is said to produce the double compound of bismuthous sulphide and bismuthic sulphotriethide.

LEAD SERIES.*—The following bodies only are known, the ethyl group alone having been explored:

* Löwig, Ann. Ch. Pharm., lxxxviii, 318; Buckton, Phil. Trans., 1859, p. 417.

Diplumbic triethide $Pb_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.$?

Plumbic oxytriethide $Pb_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\O\end{matrix}\right.$

Plumbic chlorotriethide $Pb_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\Cl\end{matrix}\right.$

Plumbic triethylosulphate $Pb_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\SO_4\end{matrix}\right.$

Plumbic ethide $Pb_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.$

The existence of the first of these bodies cannot be said to be clearly established; but by the action of an alloy of sodium and lead upon iodide of ethyl, a colourless, mobile, volatile liquid is obtained, which, when dissolved in alcohol or ether, and exposed to the air, forms plumbic oxytriethide, a body which is however more readily obtained by the decomposition of the chloride with oxide of silver:

$$\underbrace{Pb_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\Cl\end{matrix}\right.}_{\text{Plumbic chlorotriethide.}} + AgO = \underbrace{Pb_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\O\end{matrix}\right.}_{\text{Plumbic oxytriethide.}} + AgCl$$

Plumbic ethide is a colourless limpid fluid, soluble in ether, but insoluble in water, and possessing a faint odour. It is not acted upon by oxygen at ordinary temperatures, but chlorine, bromine, and iodine act violently upon it. Plumbic ethide belongs to the class of saturated bodies, and is consequently incapable of forming compounds. When it is treated with hydrochloric acid, hydride of ethyl separates and plumbic chloro-triethide is formed:

$$Pb_2\begin{cases}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{cases} + HCl = Pb_2\begin{cases}C_4H_5\\C_4H_5\\C_4H_5\\Cl\end{cases} + \left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}$$

Plumbic ethide. — Plumbic chlorotriethide. — Hydride of ethyl.

From plumbic chloro-triethide the sulphates and other salts can be prepared by double decomposition. These salts may also be obtained still more readily from the oxide, which is a crystalline, volatile, pungent body, possessing a powerful alkaline reaction, and attracting carbonic acid from the air.

MERCURIC SERIES.*—This series is confined to bodies of the mercuric type, no organo-mercurous compound having been yet produced. It comprises the following members:

Mercuric methiodide	$Hg\begin{cases}C_2H_3\\I\end{cases}$
Mercuric methhydrate	$Hg\begin{cases}C_2H_3\\H\,O_2\end{cases}$
Mercuric methonitrate	$Hg\begin{cases}C_2H_3\\N\,O_6\end{cases}$
Mercuric methide	$Hg\begin{cases}C_2H_3\\C_2H_3\end{cases}$
Mercuric ethiodide	$Hg\begin{cases}C_4H_5\\I\end{cases}$
Mercuric ethohydrate	$Hg\begin{cases}C_4H_5\\H\,O_2\end{cases}$
Mercuric ethonitrate	$Hg\begin{cases}C_4H_5\\N\,O_6\end{cases}$
Mercuric ethide	$Hg\begin{cases}C_4H_5\\C_4H_5\end{cases}$
Mercuric ethylomethide	$Hg\begin{cases}C_4H_5\\C_2H_3\end{cases}$?

Mercuric methide and mercuric ethide are colourless, ethereal, volatile liquids, insoluble in water, but insoluble in alcohol and

* Frankland, Phil. Trans., 1852, p. 436, and Phil. Trans., 1859, p. 409; Dünhaupt, Ann. Ch. Pharm., xcii, 371; Strecker, Ann. Ch. Pharm., xcii, 57; Buckton, Phil. Trans., 1858, p. 163, and 1859, p. 417.

ether, and possessing great stability. They are in a state of maximum saturation, and cannot therefore unite with any other body without the displacement of an equivalent of positive radical. Thus with bromine, mercuric ethide gives bromide of ethyl and mercuric ethylobromide:

$$\underbrace{Hg\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Mercuric ethide.}} + 2Br = \underbrace{Hg\left\{\begin{matrix}C_4H_5\\Br\end{matrix}\right.}_{\text{Mercuric ethylobromide.}} + \underbrace{\left.\begin{matrix}C_4H_5\\Br\end{matrix}\right\}}_{\text{Bromide of ethyl.}}$$

With hydrated sulphuric acid the action is:

$$\underbrace{Hg\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Mercuric ethide.}} + SO_4H = \underbrace{Hg\left\{\begin{matrix}C_4H_5\\SO_4\end{matrix}\right.}_{\text{Mercuric ethosulphate.}} + \underbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}_{\text{Hydride of ethyl.}}$$

Mercuric methide possesses the highest specific gravity of any known non-metallic liquid (3·069). Glass consequently floats upon its surface. Brought in contact with mercuric iodide, mercuric methide and mercuric ethide are converted respectively into mercuric methiodide and mercuric ethiodide:

$$\underbrace{Hg\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Mercuric methide.}} + Hg\left\{\begin{matrix}I\\I\end{matrix}\right. = \underbrace{2Hg\left\{\begin{matrix}C_2H_3\\I\end{matrix}\right.}_{\text{Mercuric methiodide.}}$$

$$\underbrace{Hg\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.}_{\text{Mercuric ethide.}} + Hg\left\{\begin{matrix}I\\I\end{matrix}\right. = \underbrace{2Hg\left\{\begin{matrix}C_4H_5\\I\end{matrix}\right.}_{\text{Mercuric ethiodide.}}$$

The reaction with mercuric chloride is exactly analogous. The hydrates of mercuric methoxide and mercuric ethoxide are caustic alkaline bases, capable of expelling ammonia from its salts, and behaving in a manner similar to the corresponding uniatomic compounds of tin and lead. The remaining mercury-compounds, which may be considered as derivatives of these two bodies, are represented in the above list by the iodides and nitrates: they generally crystallize very readily, and, with the exception of the haloïd compounds, are soluble in water. When their aqueous solutions are treated with zinc, they are decomposed, the zinc becomes amalgamated, and gaseous hydrides of the positive radicals are evolved. It is highly probable that there are two

stages in this reaction, organo-zinc compounds being first formed and then decomposed by contact with water; thus with mercuric methiodide—

$$\underbrace{2Hg\begin{cases}C_2H_3\\ I\end{cases}}_{\text{Mercuric methiodide.}} + Zn_4 = \underbrace{Zn_2\begin{cases}C_2H_3\\ C_2H_3\end{cases}}_{\text{Zinc-methyl.}} + 2ZnI + 2Hg$$

and then:

$$\underbrace{Zn_2\begin{cases}C_2H_3\\ C_2H_3\end{cases}}_{\text{Zinc-methyl.}} + \underbrace{\left.\begin{matrix}H\\ H\end{matrix}\right\} O_2}_{\text{Water.}} = \underbrace{2\left.\begin{matrix}C_2H_3\\ H\end{matrix}\right\}}_{\text{Hydride of methyl.}} + 2ZnO$$

This view of the reaction is confirmed by the fact that when zinc acts upon mercuric methiodide at 150° C., zinc-methyl is produced. When one of the above iodides or the corresponding chloride or bromide is treated with an organo-zinc compound, the negative element becomes replaced by the alcohol-radical of the zinc-compound; thus, when mercuric methiodide is treated with zinc-methyl, mercuric methide is produced. And it is believed that by acting upon mercuric ethochloride with zinc-methyl, mercuric ethylomethide is produced:

$$\underbrace{2Hg\begin{cases}C_4H_5\\ Cl\end{cases}}_{\text{Mercuric ethochloride.}} + \underbrace{Zn_2\begin{cases}C_2H_3\\ C_2H_3\end{cases}}_{\text{Zinc-methyl.}} = \underbrace{2Hg\begin{cases}C_4H_5\\ C_2H_3\end{cases}}_{\text{Mercuric ethylomethide.}} + 2ZnCl$$

but this body has not yet been obtained in a state of purity; distillation gradually resolves it into mercuric methide and mercuric ethide:

$$\underbrace{2Hg\begin{cases}C_4H_5\\ C_2H_3\end{cases}}_{\text{Mercuric ethylomethide.}} = \underbrace{Hg\begin{cases}C_2H_3\\ C_2H_3\end{cases}}_{\text{Mercuric methide.}} + \underbrace{Hg\begin{cases}C_4H_5\\ C_4H_5\end{cases}}_{\text{Mercuric ethide.}}$$

ANTIMONY SERIES.*—This important series of organo-metallic bodies contains a greater number and variety of compounds than any other, with the exception of the arsenic series. The remarkable polyatomic character of antimony and arsenic not only renders the possible number of their organo-compounds very

* Löwig, Ann. Ch. Pharm., lxxv, 315, 327; Landolt, Ann. Ch. Pharm., lxxviii, 91; Buckton, Chem. Soc. Qu. J., xiii, 115; Hofmann, *ibid*, xi, 316.

large, but the variation in the proportions of the positive and negative molecules gives an extremely wide range to their chemical character, extending, as it does, from highly caustic bases on the one hand to powerful bibasic acids on the other. The following are the principal compounds belonging to this series:

Trimethylstibine $$Sb\left\{\begin{array}{l}C_2H_3\\C_2H_3\\C_2H_3\end{array}\right.$$

Antimonic trimethoxide $$Sb\left\{\begin{array}{l}C_2H_3\\C_2H_3\\C_2H_3\\\quad O\\\quad O\end{array}\right.$$

Antimonic trimethochloride $$Sb\left\{\begin{array}{l}C_2H_3\\C_2H_3\\C_2H_3\\\quad Cl\\\quad Cl\end{array}\right.$$

Iodide of tetramethylstibonium or antimonic tetramethiodide $$Sb\left\{\begin{array}{l}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\\\quad I\end{array}\right.$$

Hydrate of tetramethylstibonium or antimonic tetramethylhydrate $$Sb\left\{\begin{array}{l}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\\H\ O_2\end{array}\right.$$ + HO

Antimonic trimethosulphate $$Sb\left\{\begin{array}{l}C_2H_3\\C_2H_3\\C_2H_3\\S\ O_4\\S\ O_4\end{array}\right.$$ O O + 2 SO3

Triethylstibine $$Sb\left\{\begin{array}{l}C_4H_5\\C_4H_5\\C_4H_5\end{array}\right.$$

Antimonic triethoxide $$Sb\left\{\begin{array}{l}C_4H_5\\C_4H_5\\C_4H_5\\\quad O\\\quad O\end{array}\right.$$

Antimonic triethochloride $Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\Cl\\Cl\end{matrix}\right.$

Iodide of tetrethylstibonium or antimonic tetramethiodide $Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\\I\end{matrix}\right.$

Iodide of methylo-triethylstibonium or antimonic triethomethiodide $Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_2H_3\\I\end{matrix}\right.$

Hydrate of tetrethylstibonium or antimonic tetrethylhydrate $Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\\H\,O_2\end{matrix}\right.$

Antimonic triethosulphate $Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\S\,O_4\\S\,O_4\end{matrix}\right.$

Sulphate of tetrethylstibonium or antimonic tetrethylsulphate $Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\\S\,O_4\end{matrix}\right.$

Antimonic triethantimonite $Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\SbO_4\\SbO_4\end{matrix}\right.$

Antimonic triethoxiodide $Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\O\\I\end{matrix}\right.$

Triamylstibine $Sb\left\{\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\\C_{10}H_{11}\end{matrix}\right.$

Antimonic triamylchloride $Sb\begin{cases} C_{10}H_{11} \\ C_{10}H_{11} \\ C_{10}H_{11} \\ Cl \\ Cl \end{cases}$

Antimonic triamylnitrate $Sb\begin{cases} C_{10}H_{11} \\ C_{10}H_{11} \\ C_{10}H_{11} \\ N\ O_6 \\ N\ O_6 \end{cases}$

It is remarkable that we have as yet no decisive evidence in this series, of the existence of a compound corresponding to cacodyl. It is true that such a body has been described under the name of *stibbiamyl,* but subsequent experiments have failed to confirm its existence. Amongst organo-antimony compounds, therefore, the most simple form is $Sb\begin{cases} R+ \\ R+ \\ R+ \end{cases}$. Bodies of this form are the analogues of ammonia, and need not be here described, since their history, and also that of bodies having the form $Sb\begin{cases} R+ \\ R+ \\ R+ \\ R+ \\ R- \end{cases}$ will be found in a discourse upon "Ammonia and its Derivatives," delivered to this Society, June 17th, 1858, by Dr. Hofmann.*

The only bodies, therefore, of this series requiring notice here are those of the form $Sb\begin{cases} R+ \\ R+ \\ R+ \\ R- \\ R- \end{cases}$, and their derivatives. When the two atoms of R— are oxygen, these compounds constitute what may be termed biacid antimony bases. They are formed either by the direct union of the stibamines $\left(Sb\begin{cases} R+ \\ R+ \\ R+ \end{cases}\right)$ with oxygen.

$$Sb\begin{cases} R+ \\ R+ \\ R+ \end{cases} + O_2 = Sb\begin{cases} R+ \\ R+ \\ R+ \\ O \\ O \end{cases}$$

* See vol. xi, p. 252, of this Journal.

or by the decomposition of the corresponding haloïd compounds by means of potash: thus—

$$\mathrm{Sb}\left\{\begin{matrix}\mathrm{R}\\\mathrm{R}\\\mathrm{R}\\\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right. + 2\mathrm{KO} = \mathrm{Sb}\left\{\begin{matrix}\mathrm{R}+\\\mathrm{R}+\\\mathrm{R}+\\\mathrm{O}\\\mathrm{O}\end{matrix}\right. + 2\mathrm{KCl}$$

The stibamines, although in other respects the perfect analogues of the nitramines, here evidently exhibit a much more highly positive character, uniting with oxygen so energetically as to be spontaneously inflammable in the lower portion of the series.

The biacid antimony bases are colourless, transparent, amorphous, and tenacious bodies; the ethyl base is easily soluble in water and alcohol, but somewhat less soluble in ether. They possess a bitter taste, are non-volatile, and do not suffer any change when exposed to the air. Treated with potassium they are reduced to stibamines:

$$\mathrm{Sb}\left\{\begin{matrix}\mathrm{R}+\\\mathrm{R}+\\\mathrm{R}+\\\mathrm{O}\\\mathrm{O}\end{matrix}\right. + 2\mathrm{K} = \mathrm{Sb}\left\{\begin{matrix}\mathrm{R}+\\\mathrm{R}+\\\mathrm{R}+\end{matrix}\right. + 2\mathrm{KO}$$

Fuming nitric acid decomposes the biacid bases with ignition; but when they are treated with dilute nitric or other acid, the respective biacid salts are produced. The oxysalts are soluble in water or alcohol; most of them crystallise without much difficulty, as do also the antimonic biniodides; but antimonic triethobromide and triethochloride are liquids not volatile without decomposition, insoluble in water, but soluble in alcohol and ether.

The existence of antimonic triethoxiodide has been recently proved by Strecker. It had previously been regarded by Merck as a protoiodide of stibethine $(\mathrm{Sb}(C_4H_5)_3I)$.

ARSENIC SERIES.*—This series is perhaps the most important and interesting amongst organo-metallic bodies; it contains the first discovered organo-metal, cacodyl, the classical investigation of

* Cadet (1760), Mém. de Math. et Phys. de Savants étrang., iii, 633; Thénard, Ann. Ch. lii, 54; Bunsen, Ann. Ch. Pharm., xxiv, 27; xxvii, 1; xlii, 14; xlvi, 1; Frankland, Ch. Soc. Qu. J., ii, 299; Cahours et Riche, Compt. rend., xxxvi, 1001; Landolt, Ann. Ch. Pharm., lxxxix, 301; Hofmann, Chem. Soc. Qu. J., xi, 316. Baeyr, Ann. Ch. Pharm. cvii, 257; cv. 265.

which by Bunsen not only imparts a completeness to our knowledge of this series, but has afforded the clue to the successful interpretation of many phenomena met with in other analogous families. It will be convenient to divide its very numerous members into three groups.

A. Organo-arsenical compounds of the type $As \begin{cases} R \\ R \end{cases}$

B. Organo-arsenical compounds of the type $As \begin{cases} R \\ R \\ R \end{cases}$

C. Organo-arsenical compounds of the type $As \begin{cases} R \\ R \\ R \\ R \\ R \end{cases}$

All arsenical compounds permit of being arranged under these three types. The following are the principal bodies already investigated:

A. Organo-arsenical Compounds of the Type $As \begin{cases} R \\ R \end{cases}$

Cacodyl	$As \begin{cases} C_2H_3 \\ C_2H_3 \end{cases}$
Ethylic cacodyl	$As \begin{cases} C_4H_5 \\ C_4H_5 \end{cases}$
Propylic cacodyl	$As \begin{cases} C_6H_7 \\ C_6H_7 \end{cases}$?
Butylic cacodyl	$As \begin{cases} C_8H_9 \\ C_8H_9 \end{cases}$?

B. Organo-arsenical Compounds of the Type $As \begin{cases} R \\ R \\ R \end{cases}$

Oxide of cacodyl	$As \begin{cases} C_2H_3 \\ C_2H_3 \\ O \end{cases}$
Sulphide of cacodyl	$As \begin{cases} C_2H_3 \\ C_2H_3 \\ S \end{cases}$
Chloride of cacodyl	$As \begin{cases} C_2H_3 \\ C_2H_3 \\ Cl \end{cases}$

Chloride of cacoplatyl $\quad \text{As}\left\{\begin{array}{l} C_2H_3 \\ C_2Pt''H \\ \quad Cl \end{array}\right.$

Arsenious dioxymethide $\quad \text{As}\left\{\begin{array}{l} C_2H_3 \\ \quad O \\ \quad O \end{array}\right.$

Arsenious disulphomethide $\quad \text{As}\left\{\begin{array}{l} C_2H_3 \\ \quad S \\ \quad S \end{array}\right.$

Arsenious dichloromethide $\quad \text{As}\left\{\begin{array}{l} C_2H_3 \\ \quad Cl \\ \quad Cl \end{array}\right.$

Trimethylarsine $\quad \text{As}\left\{\begin{array}{l} C_2H_3 \\ C_2H_3 \\ C_2H_3 \end{array}\right.$

Arsenious diethiodide $\quad \text{As}\left\{\begin{array}{l} C_4H_5 \\ C_4H_5 \\ \quad I \end{array}\right.$

Triethylarsine $\quad \text{As}\left\{\begin{array}{l} C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{array}\right.$

C. Organo-arsenical Compounds of the Type $\text{As}\left\{\begin{array}{l} R \\ R \\ R \\ R \\ R \end{array}\right.$

This group may be conveniently divided into four families or sub-types, viz.:

a. Bodies of the form $\text{As}\left\{\begin{array}{l} R+ \\ R- \\ R- \\ R- \\ R- \end{array}\right.$, and their derivatives.

b. Bodies of the form $\text{As}\left\{\begin{array}{l} R+ \\ R+ \\ R- \\ R- \\ R- \end{array}\right.$, and their derivatives.

c. Bodies of the form $\text{As}\left\{\begin{array}{l} R+ \\ R\div \\ R+ \\ R- \\ R- \end{array}\right.$, and their derivatives.

d. Bodies of the form $As \begin{cases} R+ \\ R+ \\ R+ \\ R+ \\ R- \end{cases}$

a. Sub-type $As \begin{cases} R+ \\ R- \\ R- \\ R- \\ R- \end{cases}$

Monomethylarsenic acid $As \begin{cases} C_2H_3 \\ O \\ O \\ O \\ O \end{cases}$

Monomethylarseniates $As \begin{cases} C_2H_3 \\ O \\ O \\ MO_2 \\ MO_2 \end{cases}$

Arsenic dioxydichlormethide $As \begin{cases} C_2H_3 \\ O \\ O \\ Cl \\ Cl \end{cases}$

Arsenic tetrachlormethide $As \begin{cases} C_2H_3 \\ Cl \\ Cl \\ Cl \\ Cl \end{cases}$

b. Sub-type $As \begin{cases} R+ \\ R+ \\ R- \\ R- \\ R- \end{cases}$

Cacodylic Acid $As \begin{cases} C_2H_3 \\ C_2H_3 \\ O \\ O \\ O \end{cases}$

Cacodylates $As \begin{cases} C_2H_3 \\ C_2H_3 \\ O \\ O \\ M\,O_2 \end{cases}$

Sulphocacodylic acid $As \begin{cases} C_2H_3 \\ C_2H_3 \\ S \\ S \\ S \end{cases}$

Sulphocacodylates $As \begin{cases} C_2H_3 \\ C_2H_3 \\ S \\ S \\ M\,S_2 \end{cases}$

Terchloride of cacodyl $As \begin{cases} C_2H_3 \\ C_2H_3 \\ Cl \\ Cl \\ Cl \end{cases}$

Ethyl-cacodylic acid $As \begin{cases} C_4H_5 \\ C_4H_5 \\ O \\ O \\ O \end{cases}$

Ethyl-cacodylates $As \begin{cases} C_4H_5 \\ C_4H_5 \\ O \\ O \\ M\,O_2 \end{cases}$

c. Sub-type $As \begin{cases} R+ \\ R+ \\ R+ \\ R- \\ R- \end{cases}$

Arsenic triethoxide $As \begin{cases} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ O \\ O \end{cases}$

Arsenic triethosulphate $As\left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ S\ O_4 \\ S\ O_4 \end{matrix}\right.$

Arsenic triethosulphide $As\left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ S \\ S \end{matrix}\right.$

Arsenic triethochloride $As\left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ Cl \\ Cl \end{matrix}\right.$

d. Bodies of the form $As\left\{\begin{matrix} R+ \\ R+ \\ R+ \\ R+ \\ R- \end{matrix}\right.$

Oxide of tetramethylarsonium or arsenic tetramethoxide $As\left\{\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ O \end{matrix}\right.$

Sulphate of tetramethylarsonium or arsenic tetramethylsulphate $As\left\{\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ SO_4 \end{matrix}\right.$

Iodide of tetramethylarsonium or arsenic tetramethiodide $As\left\{\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ I \end{matrix}\right.$

Oxide of dimethyl-diethylarsonium or arsenic dimethyl-diethyloxide $As\left\{\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_4H_5 \\ C_4H_5 \\ O \end{matrix}\right.$

Iodide of dimethyl-diethylarsonium
or arsenic dimethyl-diethyliodide

$$As\left\{\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_4H_5 \\ C_4H_5 \\ I \end{matrix}\right.$$

Nitrate of dimethyl-diethylarsonium
or arsenic dimethyl-diethylnitrate

$$As\left\{\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_4H_5 \\ C_4H_5 \\ N\,O_6 \end{matrix}\right.$$

Oxide of tetrethylarsonium
or arsenic tetrethoxide

$$As\left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ O \end{matrix}\right.$$

Sulphate of tetrethylarsonium
or arsenic tetrethylsulphate

$$As\left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ S\,O_4 \end{matrix}\right.$$

Chloride of tetrethylarsonium
or arsenic tetrethylchloride

$$As\left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ Cl \end{matrix}\right.$$

Iodide of dimethyl-diamylarsonium
or arsenic diamyliodide

$$As\left\{\begin{matrix} C_2\,H_3 \\ C_2\,H_3 \\ C_{10}H_{11} \\ C_{10}H_{11} \\ I \end{matrix}\right.$$

The organo-arsenical compounds belonging to the type $As\left\{\begin{matrix} R \\ R \end{matrix}\right.$ contain only positive radicals. They are volatile poisonous liquids, insoluble in water, but very soluble in alcohol and ether, and possessing an insupportable odour. The lower members of the family are spontaneously inflammable, whilst the higher ones also rapidly oxidise in air. They unite with negative elements with great energy, manifesting in their combinations either a uniatomic or a teratomic character, and producing bodies either of the form $As\left\{\begin{matrix} R+ \\ R+ \\ R- \end{matrix}\right.$ or $As\left\{\begin{matrix} R+ \\ R+ \\ R- \\ R- \\ R- \end{matrix}\right.$. Thus cacodyl forms with chlorine, chloride of cacodyl and terchloride of cacodyl.

$$\underbrace{As\begin{cases}C_2H_3\\C_2H_3\end{cases}}_{\text{Cacodyl.}} + Cl = \underbrace{As\begin{cases}C_2H_3\\C_2H_3\\Cl\end{cases}}_{\text{Chloride of cacodyl.}}$$

$$\underbrace{As\begin{cases}C_2H_3\\C_2H_3\end{cases}}_{\text{Cacodyl.}} + Cl_3 = \underbrace{As\begin{cases}C_2H_3\\C_2H_3\\Cl\\Cl\\Cl\end{cases}}_{\text{Terchloride of cacodyl.}}$$

Methylic cacodyl boils at 170° C., and ethylic cacodyl between 185° and 190° C.

Heated to 400° C., cacodyl splits up into metallic arsenic, hydride of methyl, and olefiant gas:

$$\underbrace{2As\begin{cases}C_2H_3\\C_2H_3\end{cases}}_{\text{Cacodyl.}} = As_2 + \underbrace{2\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}}_{\text{Hydride of methyl.}} + \underbrace{C_4H_4}_{\text{Olefiant gas.}}$$

Bodies of this type can be regenerated by reducing agents from many of their uniatomic compounds; thus chloride of cacodyl and metallic zinc give cacodyl and chloride of zinc:

$$\underbrace{As\begin{cases}C_2H_3\\C_2H_3\\Cl\end{cases}}_{\text{Chloride of cacodyl.}} + Zn = \underbrace{As\begin{cases}C_2H_3\\C_2H_3\end{cases}}_{\text{Cacodyl.}} + ZnCl$$

Organo-arsenical compounds of the type $As\begin{cases}R\\R\\R\end{cases}$ are of three forms, viz.:

$$(1)\quad As\begin{cases}R+\\R+\\R+\end{cases}\qquad (2)\quad As\begin{cases}R+\\R+\\R-\end{cases}\qquad (3)\quad As\begin{cases}R+\\R-\\R-\end{cases}$$

Those belonging to the first are termed *arsines*, and are the analogues of ammonia; but, like the corresponding antimony compounds, in addition to their alkaloid function, they have the power of combining with two negative atoms, forming bodies of the sub-type $As\begin{cases}R+\\R+\\R+\\R-\\R-\end{cases}$. Thus triethylarsine combines with oxygen to form arsenic dioxytriethide. The lower members of the type

possess this property to such an extent as to render them spontaneously inflammable in air.

Compounds belonging to the second of the above forms are produced by the direct combination of the cacodyls with negative elements, the oxides are bases of comparatively feeble power, slowly combining with two additional equivalents of oxygen, to form acids. Thus oxide of cacodyl, by exposure to air, slowly passes into cacodylic acid:

$$\underbrace{As\left\{\begin{matrix}C_2H_3\\C_2H_3\\O\end{matrix}\right.}_{\text{Oxide of cacodyl.}} + O_2 = \underbrace{As\left\{\begin{matrix}C_2H_3\\C_2H_3\\O\\O\\O\end{matrix}\right.}_{\text{Cacodylic acid.}}$$

The chlorine, bromine, and iodine compounds of the form we are now considering are volatile neutral bodies, which may be regarded as the haloïd salts of cacodyl. Heated in contact with bichloride of platinum, the chloride of cacodyl presents an interesting re-action; two equivalents of hydrogen in the cacodyl become replaced by a biatomic molecule of platinum, producing chloride of cacoplatyl.

$$\underbrace{As\left\{\begin{matrix}C_2H_3\\C_2H_3\\Cl\end{matrix}\right.}_{\text{Chloride of cacodyl.}} + PtCl_2 = \underbrace{As\left\{\begin{matrix}C_2H_3\\C_2Pt''H\\Cl\end{matrix}\right.}_{\text{Chloride of cacoplatyl.}} + 2HCl$$

Cacoplatyl forms a series of compounds analogous to those of cacodyl.

The only compounds of the third form yet known belong to the methylic group. Arsenious dioxymethide is a crystalline body of a neutral character, soluble in water, alcohol, and ether, unchanged by exposure to air, but transformed by distillation with hydrate of potash into arsenious acid and oxide of cacodyl:

$$\underbrace{2\,As\left\{\begin{matrix}C_2H_3\\O\\O\end{matrix}\right.}_{\text{Arsenious dioxymethide.}} = As\,O_3 + \underbrace{As\left\{\begin{matrix}C_2H_3\\C_2H_3\\O\end{matrix}\right.}_{\text{Oxide of cacodyl.}}$$

Hydrochloric acid converts it into arsenious dichlormethide:

$$\underbrace{As\left\{\begin{matrix}C_2H_3\\O\\O\end{matrix}\right.}_{\text{Arsenious dioxymethide.}} + 2HCl = \underbrace{As\left\{\begin{matrix}C_2H_3\\Cl\\Cl\end{matrix}\right.}_{\text{Arsenious dichlormethide.}} + \left.\begin{matrix}H\\H\end{matrix}\right\}O_2$$

Hydrobromic and hydriodic acids produce a perfectly analogous change, whilst sulphuretted hydrogen tranforms it into arsenious disulphomethide. The chloric compound can also be formed by heating arsenic trichlormethide to 50° C.

$$\underbrace{As\left\{\begin{matrix}C_2H_3\\C_2H_3\\Cl\\Cl\\Cl\end{matrix}\right.}_{\text{Arsenic trichlormethide.}} = \underbrace{As\left\{\begin{matrix}C_2H_3\\Cl\\Cl\end{matrix}\right.}_{\text{Arsenious dichlormethide.}} + \underbrace{\left.\begin{matrix}C_2H_3\\Cl\end{matrix}\right\}}_{\text{Chloride of methyl.}}$$

The chlorine, bromine, and iodine compounds are neutral bodies of considerable stability; the two former are liquid, the latter solid and crystalline. By the action of chlorine or oxidising agents, they are transformed into bodies of the form $As\left\{\begin{matrix}R & +\\R & -\\R & -\\R & -\\R & -\end{matrix}\right.$

Organo-arsenical compounds have been more thoroughly investigated in the direction of the type $As\left\{\begin{matrix}R\\R\\R\\R\\R\end{matrix}\right.$ than in any other; consequently we find these bodies rather numerously represented, especially under the subtype $As\left\{\begin{matrix}R & +\\R & +\\R & +\\R & +\\R & -\end{matrix}\right.$. As the latter bodies, however, are the strict analogues of the compounds of ammonium, their chemical relations will be found fully described in Dr. Hofmann's discourse before alluded to,

Sub-type $As\left\{\begin{matrix}R & +\\R & -\\R & -\\R & -\\R & -\end{matrix}\right.$ has only yet been explored in the methylic group. The oxygen-compound constitutes anhydrous monomethylarsenic acid, a direct derivative from arsenious dioxymethide:

$$\underset{\text{Arsenious dioxymethide.}}{\underline{As\left\{\begin{matrix}C_2H_3\\O\\O\end{matrix}\right.}} + 2\,AgO = \underset{\text{Monomethylarsenic acid.}}{\underline{As\left\{\begin{matrix}C_2H_3\\O\\O\\O\\O\end{matrix}\right.}} + 2\,Ag$$

This acid is bibasic, forming stable and well defined crystallisable salts, the formulæ of which are represented by the general expression

$$As\left\{\begin{matrix}C_2H_3\\O\\O\\MO_2\\MO_2\end{matrix}\right.$$

The chlorine compound is exceedingly unstable; it may however be formed at $-10°C.$, but is transformed at $0°C.$ into arsenious chloride and chloride of methyl:

$$\underset{\text{Arsenic tetrachlormethide.}}{\underline{As\left\{\begin{matrix}C_2H_3\\Cl\\Cl\\Cl\\Cl\end{matrix}\right.}} = As\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right. + \underset{\text{Chloride of methyl.}}{\underline{\left.\begin{matrix}C_2H_3\\Cl\end{matrix}\right\}}}$$

Arsenic dioxydichlormethide is a somewhat more stable body formed by the direct union of chlorine with arsenious dioxymethide.

$$\underset{\text{Arsenious dioxymethide.}}{\underline{As\left\{\begin{matrix}C_2H_3\\O\\O\end{matrix}\right.}} + Cl_2 = \underset{\text{Arsenic dioxydichlormethide.}}{\underline{As\left\{\begin{matrix}C_2H_3\\O\\O\\Cl\\Cl\end{matrix}\right.}}$$

Nevertheless, even this compound readily decomposes, with evolution of chloride of methyl.

Sub-type $As\left\{\begin{matrix}R & +\\R & +\\R & -\\R & -\\R & -\end{matrix}\right.$ The oxygen-compounds are feeble monobasic acids of which cacodylic acid may be regarded as the representative. They are derived from the bodies $As\left\{\begin{matrix}R & +\\R & +\\O & \end{matrix}\right.$ by direct

oxidation as already described. Cacodylic acid is remarkable for its stability; neither fuming nitric acid nor a mixture of sulphuric; and chromic acids attack it, even at the boiling point, and it may be heated to 200° C. without alteration. Although it is soluble in water and contains upward of 54 per cent. of arsenic, yet it is not in the least poisonous. Several agents reduce cacodylic acid to the arsenious or even to the diatomic form. Thus phosphorous acid transforms it into cacodyl:

$$\underbrace{2\,As\left\{\begin{matrix}C_2H_3\\C_2H_3\\O\\O\\O\end{matrix}\right.}_{\text{Cacodylic acid.}} + 3\,P\left\{\begin{matrix}O\\O\\O\end{matrix}\right. = \underbrace{2\,As\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.}_{\text{Cacodyl.}} + 3\,PO_5$$

Zinc also produces the same result. Hydriodic acid gas converts cacodylic acid into arsenious dimethiodide:

$$As\left\{\begin{matrix}C_2H_3\\C_2H_3\\O\\O\\O\end{matrix}\right. + 3\,HI = As\left\{\begin{matrix}C_2H_3\\C_2H_3\\I\end{matrix}\right. + I_2 + 3\,HO$$

The acid character of this body is so slightly marked as to render it capable of forming compounds in which it appears to play the part of a base. Thus with hydrofluoric, hydrochloric and hydrobromic acids, it forms the following compounds:

Hydrofluate of cacodylic acid $As\left\{\begin{matrix}C_2H_3\\C_2H_3\\H\,O_2\\H\,O_2\\F\end{matrix}\right.$

Hydrochlorate of cacodylic acid $As\left\{\begin{matrix}C_2H_3\\C_2H_3\\H\,O_2\\H\,O_2\\Cl\end{matrix}\right.$

Hydrobromate of cacodylic acid $As\left\{\begin{matrix}C_2H_3\\C_2H_3\\H\,O_2\\H\,O_2\\Br\end{matrix}\right.$

The hydrobromate reacts perfectly neutral. The cacodylates have the formula:

$$As\left\{\begin{matrix} C_2H_3 \\ C_2H_3 \\ O \\ O \\ MO_2 \end{matrix}\right.$$

Sulphocacodylic acid has not yet been isolated, but its salts present the same relations to those of cacodylic acid, as salts of sulphur-acids generally bear to those of oxyacids. Their formula is

$$As\left\{\begin{matrix} C_2H_3 \\ C_2H_3 \\ S \\ S \\ MS_2 \end{matrix}\right.$$

Sub-type $As\left\{\begin{matrix} R & + \\ R & + \\ R & + \\ R & - \\ R & - \end{matrix}\right.$ has hitherto been very little explored, so far as it is known, but its members bear so close a resemblance to their analogues in the antimony-series, as to require no further notice.

Tellurium series.* The close relations of tellurium to sulphur and selenium place the bodies of this series in the same position with regard to the sulphides and selenides of the alcohol-radicals as the antimony and arsenic series stand in relation to the corresponding compounds of phosphorus and nitrogen.

The following bodies belonging to this series are known:

Tellurium methyl	$Te_2\left\{\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right.$
Tellurous dimethoxide	$Te_2\left\{\begin{matrix} C_2H_3 \\ C_2H_3 \\ O \\ O \end{matrix}\right.$
Tellurous methoxychloride	$Te_2\left\{\begin{matrix} C_2H_3 \\ C_2H_3 \\ O \\ Cl \end{matrix}\right.$

* Wöhler, Ann. Ch. Pharm., xxxv, 112, lxxxiv, 69; Mallet, Ann. Ch. Pharm., lxxix, 223; Wöhler and Dean, Ann. Ch. Pharm., xciii, 233.

Tellurous dimethiodide	$Te_2 \begin{cases} C_2H_3 \\ C_2H_3 \\ I \\ I \end{cases}$
Tellurium-ethyl	$Te_2 \begin{cases} C_4H_5 \\ C_4H_5 \end{cases}$
Tellurous diethoxide	$Te_2 \begin{cases} C_4H_5 \\ C_4H_5 \\ O \\ O \end{cases}$
Tellurous diethosulphide	$Te_2 \begin{cases} C_4H_5 \\ C_4H_5 \\ S \\ S \end{cases}$
Acid tellurous diethosulphate	$Te_2 \begin{cases} C_4H_5 \\ C_4H_5 \\ HO_2 \\ SO_4 \end{cases}$
Tellurous diethochloride	$Te_2 \begin{cases} C_4H_5 \\ C_4H_5 \\ Cl \\ Cl \end{cases}$
Tellurous diethoxychloride	$Te_2 \begin{cases} C_4H_5 \\ C_4H_5 \\ Cl \\ O \end{cases}$
Tellurous diethiodide	$Te_2 \begin{cases} C_4H_5 \\ C_4H_5 \\ I \\ I \end{cases}$
Tellurium-amyl	$Te_2 \begin{cases} C_{10}H_{11}? \\ C_{10}H_{11} \end{cases}$

The compounds of the alcohol-radicals with tellurium are volatile liquids of most unbearable odour. They oxidise readily in contact with air, forming the respective oxides. Tellurium-amyl has not yet been obtained in a state of purity.

The oxides of these bodies are powerful bases, expelling ammonia from its salts, and attracting carbonic acid from the air. They form salts of considerable stability, which, as well as the oxides themselves, yield the original organo-tellurium compounds when treated with sulphurous acid:

$$Te_2 \begin{cases} C_4H_5 \\ C_4H_5 \\ O \\ O \end{cases} + S_2O_4 = Te_2 \begin{cases} C_4H_5 \\ C_4H_5 \end{cases} + S_2O_6$$

Tellurous diethoxide. Tellurium ethyl.

Constitution, and Theoretical Importance of Organo-metallic Bodies.

In the year 1852*, at a time when comparatively little progress had been made in the investigation of organo-metallic bodies, I ventured to propose a view of their constitution which further research has completely confirmed. According to this view, the organo-metallic bodies are constructed upon the types of the inorganic chlorides, sulphides, oxides, &c., of the respective metals which they contain, the chlorine, oxygen, sulphur, &c., being replaced in equivalent proportion and step by step by the alcohol-radicals.

A reference to the formulæ of organo-potassium, sodium, magnesium, zinc, and cadmium compounds given above, shows that they are all formed upon the models of the protochlorides of these metals; the general type being

$$M_2 \begin{cases} Cl \\ Cl \end{cases}$$

In like manner organo-aluminium compounds are formed upon the type of the sesquichloride of that metal:

$$Al_2 \begin{cases} Cl \\ Cl \\ Cl \end{cases}$$

Organo-tin compounds are represented by the three chlorides of tin:

$$Sn_2 \begin{cases} Cl \\ Cl \end{cases} \qquad Sn_2 \begin{cases} Cl \\ Cl \\ Cl \end{cases} \qquad Sn_2 \begin{cases} Cl \\ Cl \\ Cl \\ Cl \end{cases}$$

The compounds of the bismuth-series are represented by the terchloride of bismuth and by bismuthic acid:

$$Bi \begin{cases} Cl \\ Cl \\ Cl \end{cases} \qquad Bi \begin{cases} O \\ O \\ O \\ O \\ O \end{cases}$$

* Phil. Trans. for 1852, p. 438.

Organo-lead compounds are arranged under the types of sesquioxide and peroxide of lead :

$$Pb_2 \begin{cases} O \\ O \\ O \end{cases} \qquad Pb_2 \begin{cases} O \\ O \\ O \\ O \end{cases}$$

The mercury-series are all moulded upon the type of the bichloride :

$$Hg \begin{cases} Cl \\ Cl \end{cases}$$

The *arsenic* and *antimony* series have for their types the following inorganic compounds :

$$As \begin{cases} S \\ S \end{cases}, \quad As \begin{cases} Cl \\ Cl \\ Cl \end{cases}, \quad As \begin{cases} O \\ O \\ O \\ O \\ O \end{cases}, \quad Sb \begin{cases} Cl \\ Cl \\ Cl \end{cases}, \quad Sb \begin{cases} Cl \\ Cl \\ Cl \\ Cl \\ Cl \end{cases}$$

The inorganic models for the tellurium series are chloride of tellurium and tellurous acid :

$$Te_2 \begin{cases} Cl \\ Cl \end{cases} \qquad Te_2 \begin{cases} O \\ O \\ O \\ O \end{cases}$$

Occasionally an abnormal compound has made its appearance, such as ethostibilic acid ($Sb\ (C_4\ H_5)\ 0_5$) or iodide of triethylstibine ($Sb\ (C_4\ H_5)_3\ J$); but further research has invariably demonstrated the incorrectness of such formulæ and the conformity of the bodies with the normal inorganic types. Indeed this law may now be regarded as sufficiently established to be applicable to the control of the formulæ of new organo-metallic bodies.

From the point of view thus afforded, it is interesting to watch the effect of the substitution in metallic compounds, of basylous or positive for chlorous or negative radicals. Such a substitution affords striking evidence of the dependence of the chemical character of a compound upon that of each individual constituent. The highly polyatomic metals, such as arsenic and antimony, exhibit this dependence in the most conclusive manner. Thus tribasic arsenic acid, by the substitution of an equivalent of methyl for oxygen, yields the bibasic monomethyl-arsenic acid, a well defined acid of considerable energy, though inferior in chlorous power to arsenic acid. The like substitution of a second equivalent of methyl for

oxygen, reduces the chlorous character of the body to the comparatively feeble condition in which we find it in cacodylic acid, which is incapable of forming an ammonia-salt. A similar substitution for the third time, overpowers the acid attribute of the compound altogether, and we now have a feeble biacid base, the arsenic dioxymethide, which again, by the exchange of a fourth atom of oxygen for methyl, is transformed into the oxide of tetramethylarsonium, a base of such energy, as to be comparable with the caustic alkalies themselves.

The behaviour of the organo-metallic bodies teaches a doctrine which affects chemical compounds in general, and which may be called the doctrine of atomic saturation; each element is capable of combining with a certain limited number of atoms; and this number can never be exceeded, although the energy of its affinities may have been increased by combination up to this point. Thus zinc appears to attain its atomic saturation by uniting with only one atom of another body; in other words, it is uniatomic, consequently the zinc compounds of the alcohol-radicals, notwithstanding their intense affinities, are incapable of direct union with other bodies. The action of chlorous elements upon them is apparently one of substitution not of combination. Polyatomic metals exhibit the same phenomenon. A double atom of tin cannot combine with more than four atoms; a single atom of arsenic or antimony with more than five atoms of other bodies; but in the combinations of polyatomic metals, we frequently notice from the lowest to the highest compound one or more intermediate points of exalted stability; thus antimony has a teratomic stage of comparative stability; nitrogen, phosphorus, and arsenic, whilst exhibiting a similar teratomic stage, have also a biatomic one, though of greatly inferior stability; whilst the existence of protoxide of nitrogen renders it more than probable that nitrogen has a third and uniatomic stage.

In bodies possessing at least one stage of stability below saturation, and in which all the atoms united with the polyatomic element are of the same kind, the stage of maximum stability is very rarely that of saturation. Thus in nitrogen, arsenic, and bismuth compounds of the kind just mentioned, the stage of maximum stability is decidedly the teratomic one; in antimonial compounds of a similar nature the teratomic is also, though less decidedly, the stage of maximum stability, whilst in phosphorous compounds the

points of maximum stability and of saturation generally coincide. When, however, the atoms united with the polyatomic element are not of the same kind, then the stage of maximum stability usually coincides with that of saturation. Thus the binoxide or bichloride of triethylarsine or triethylstibine are more stable than triethylarsine, or triethylstibine themselves; but this pentatomic stability reaches its climax in arsonium, stibonium, and phosphonium compounds, as it does also in the corresponding compounds of nitrogen, although the latter element exhibits a much stronger tendency towards universal teratomic stability than its chemical associates.

In polyatomic organo-metallic bodies, it is remarkable that, with few exceptions, the positive hydrocarbons hold their position much more tenaciously than the associated negative constituents; and we thus frequently find the former accompanying the metal through a vast number of compounds. Hence the group formed by the metal and positive hydrocarbons has come to be regarded as a compound radical. Thus cacodyl is conceived to be the radical of the whole series of cacodyl compounds. But however great may be the convenience of this mode of viewing organo-metallic compounds, and the same mode has notoriously been extended to nearly all organic bodies, it must not be forgotten that it is a purely artificial distinction, which has no real existence, either in the case of organo-metallic bodies, or, as I shall endeavour to show, in that of organic bodies in general.

A close examination of the habits of the so-called organo-metallic radicals shows clearly, that their atomic power depends upon their position with regard to the stages of stability and maximum saturation; thus they are uniatomic when the number of positive groups is one less than that required to reach either the maximum saturation of the metal, or a lower stage of stability. Cacodyl and tetramethyl-arsonium, for instance, are uniatomic radicals, because they are respectively one atom short of the stage of stability, and of maximum saturation:

Uniatomic stage.	Stage of stability.
$As \begin{cases} C_2H_3 \\ C_2H_3 \end{cases}$	$As \begin{cases} C_2H_3 \\ C_2H_3 \\ Cl \end{cases}$
Cacodyl.	Chloride of cacodyl.

Uniatomic stage.	Stage of maximum saturation.
$As\begin{cases}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\end{cases}$	$As\begin{cases}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\\Cl\end{cases}$
Tetramethylarsonium.	Chloride of tetramethylarsonium.

It is obvious that a compound radical, the number of whose positive atoms is below that of a stage of stability, can have a double atomic character. Thus cacodyl is sometimes uniatomic, as in oxide of cacodyl; and sometimes teratomic, as in cacodylic acid. Again arsenio-monomethyl (AsC_2H_3) is biatomic in arsenious dioxymethide:

$$As\begin{cases}C_2H_3\\O\\O\end{cases}$$

and quadratomic in monomethylarsenic acid:

$$As\begin{cases}C_2H_3\\O\\O\\O\\O\end{cases}$$

If these views of the constitution and character of organo-metallic bodies and their compounds be correct, their application to the organic compounds of carbon becomes inevitable. Regarded from this point of view, the double atom of carbon, like that of tin, is quadratomic in perchloride of carbon and carbonic acid:

$C_2\begin{cases}Cl\\Cl\\Cl\\Cl\end{cases}$	$C_2\begin{cases}O\\O\\O\\O\end{cases}$
Perchloride of carbon.	Carbonic acid.

and biatomic in protochloride of carbon and carbonic oxide:

$C_2\begin{cases}Cl\\Cl\end{cases}$	$C_2\begin{cases}O\\O\end{cases}$
Protochloride of carbon.	Carbonic oxide.

In other words, the quadratomic stage in carbon-compounds is the stage of maximum saturation, whilst the biatomic stage is one of exalted stability. If we substitute an atom of chlorine in per-

chloride of carbon by one of ethyl, we produce a body having the formula of trichlorhydrin:

$$C_2\left\{\begin{matrix} C_4H_5 \\ Cl \\ Cl \\ Cl \end{matrix}\right.$$

If now a second atom of chlorine be substituted by one of hydrogen, we have a body exhibiting the composition of bichloride of propylene:

$$C_2\left\{\begin{matrix} C_4H_5 \\ H \\ Cl \\ Cl \end{matrix}\right.$$

This view of the constitution of bichloride of propylene renders its relations to allyl and glycerin compounds at once simple and intelligible.

The substitution of a third atom of hydrogen gives the formula of chloride of propyl:

$$C_2\left\{\begin{matrix} C_4H_5 \\ H \\ H \\ Cl \end{matrix}\right.$$

whilst the substitution of the last atom of chlorine by hydrogen yields hydride of propyl, and its replacement by ethyl yields the so-called double radical ethylpropyl. It still remains for experiment to produce these bodies from perchloride of carbon, and to show that they are identical with the known compounds possessing the same percentage composition.* If, however, we turn to the oxygen-compounds of carbon, we are not entirely without experimental evidence of the correctness of this view; since one atom of oxygen in carbonic acid has been replaced by ethyl, with production of the body theoretically indicated, namely propionic acid:

$$C_2\left\{\begin{matrix} C_4H_5 \\ O \\ O \\ O \end{matrix}\right.$$

Could a second atom of oxygen be substituted by hydrogen, we ought to produce propionic aldehyde:

$$C_2\left\{\begin{matrix} C_4H_5 \\ H \\ O \\ O \end{matrix}\right.$$

* Such experiments are in progress, but are not sufficiently advanced to be here quoted.

The replacement of a third atom of oxygen by hydrogen would then yield propylic ether:

$$C_2\begin{cases} C_4H_5 \\ H \\ H \\ O \end{cases}$$

whilst the replacement of the last atom of oxygen by hydrogen should give rise to hydride of propyl, and by uniatomic peroxide of hydrogen, to propylic alcohol:

$$\underbrace{C_2\begin{cases} C_4H_5 \\ H \\ H \\ H \end{cases}}_{\text{Hydride of propyl.}} \qquad \underbrace{C_2\begin{cases} C_4H_5 \\ H \\ H \\ HO_2 \end{cases}}_{\text{Propylic alcohol.}}$$

The glycols, are also constructed upon the carbonic acid type:

$$\underbrace{C_2\begin{cases} C_2H_3 \\ H \\ HO_2 \\ HO_2 \end{cases}}_{\text{Glycol.}}$$

and to the same type belongs also the teracid alcohol, glycerin.

$$C_2\begin{cases} C_4H_5 \\ HO_2 \\ HO_2 \\ HO_2 \end{cases}$$

Under the influence of iodide of phosphorus, glycerin yields iodide of allyl:

$$\underbrace{C_2\begin{cases} C_4H_5 \\ HO_2 \\ HO_2 \\ HO_2 \end{cases}}_{\text{Glycerin.}} + P\begin{cases} I \\ I \\ I \end{cases} = \underbrace{C_2\begin{cases} C_4H_5 \\ I \end{cases}}_{\text{Iodide of allyl.}} + \underbrace{P\begin{cases} O \\ O \\ HO_2 \\ HO_2 \\ HO_2 \end{cases}}_{\text{Phosphoric acid.}} + I_2$$

Here we have a reduction from the carbonic acid to the carbonic oxide type, of precisely the same nature as that which occurs when cacodylic acid is reduced to oxide of cacodyl. Allylic compounds are therefore constructed upon the carbonic oxide type.

$$\underset{\text{Carbonic oxide.}}{C_2\left\{\begin{matrix}O\\O\end{matrix}\right.}\quad,\qquad \underset{\text{Iodide of allyl.}}{C_2\left\{\begin{matrix}C_4H_5\\I\end{matrix}\right.}\quad,\qquad \underset{\text{Allylic alcohol.}}{C_2\left\{\begin{matrix}C_4H_5\\HO_2\end{matrix}\right.}$$

It would be easy greatly to extend this view of the constitution of organic carbon compounds; but the above examples are sufficient to indicate its general application somewhat more fully than I have previously done,* and more than this is not desirable until the hypothesis has been further supported by experimental results.

In conclusion, it is evident that this is only one mode of applying to organic compounds the law of chemical combination which I have endeavoured to deduce from the constitution and behaviour of organo-metallic bodies. Its application ought to be, and will be found to be, equally truthful in referring organic compounds containing hydrogen, oxygen, or nitrogen, to the inorganic typical compounds of each of these elements. Thus, for example, we can represent alcohol:

1st, as derived from carbonic acid:

$$C_2\left\{\begin{matrix}C_2H_3\\H\\H\\HO_2\end{matrix}\right.$$

2nd, as derived from teroxide of hydrogen:

$$H\left\{\begin{matrix}C_4H_5\\O\\O\end{matrix}\right. = H\left\{\begin{matrix}C_2\left\{\begin{matrix}C_2H_3\\H\\H\end{matrix}\right.\\O\\O\end{matrix}\right.$$

3rd, as derived from water:

$$O_2\left\{\begin{matrix}C_4H_5\\H\end{matrix}\right. = O_2\left\{\begin{matrix}C_2\left\{\begin{matrix}C_2H_3\\H\\H\end{matrix}\right.\\H\end{matrix}\right.$$

In like manner, nitrogen compounds and their analogues, whilst derived from typical inorganic compounds of nitrogen, are also

* Ann. Ch. Pharm., ci, 260; Proc. of Royal Inst. of Great Britain for 1858. It is highly remarkable that more than thirteen years ago, when such analogies were of the most obscure kind, the quick perception of Liebig led him to point out analogous relations between carbonic acid, alcohol, formic acid, and marsh gas. See Ann. Ch. Pharm., lviii, 335.)

true derivatives from the carbon types. Thus trimethylamine is correctly written as a derivative from carbonic acid :

$$C_2 \begin{cases} N\,(C_2H_3)_2 \\ H \\ H \\ H \end{cases}$$

Each of these modes of notation is equally correct; but I conceive that a large number of those organic bodies, which are usually formulated in accordance with the hydrogen, water, and hydrochloric acid models, would be much more usefully expressed upon the carbonic acid and carbonic oxide types. The formulation of organic compounds is not a matter of indifference, even to the chemical investigator; and hence every mode of expression founded upon broad chemical relations ought to have the preference over more purely artificial methods.

XX.—*On Acetoxybenzamic Acid, an Isomer of Hippuric Acid.*

By G. C. Foster.

If we regard hippuric acid as benzoyl-glycocol, or glycocol in which an atom of hydrogen is replaced by benzoyl, it seems natural to expect that an acid isomeric with, and analogous to, hippuric acid, might be obtained by replacing an atom of hydrogen in oxybenzamic acid (syn. benzamic acid, amidobenzoic acid) by acetyl. From the results recorded in this paper, it appears that such is the case.

When oxybenzamic acid is heated in a sealed tube with about half its weight (rather more than one equivalent) of monohydrated acetic acid, the whole mass becomes quite fluid at about 130° or 140°C. but solidifies almost entirely at about 160°, all that remains

liquid being the portion of acetic acid used in excess. The reaction which takes place is the following:—

$$\underset{\text{Oxybenzamic acid.}}{C_7H_7NO_2} + \underset{\text{Acetic acid.}}{C_2H_4O_2} = \underset{\text{Acetoxybenzamic acid.}}{C_9H_9NO_3} + H_2O.^*$$

Using at a time from 15 to 20 grammes of oxybenzamic acid, I found that the reaction was quite complete after an hour's heating to 160°, especially if advantage had been taken of the period of complete liquefaction to mix the materials thoroughly.

The same product is also formed by the reaction of chloride of acetyl on oxybenzamate of zinc† at 100°:

$$\underset{\text{Oxybenzamate of zinc.}}{C_7H_6ZnNO_2} + \underset{\text{Chloride of acetyl.}}{C_2H_3OCl} = \underset{\text{Acetoxybenzamic acid.}}{C_9H_9NO_3} + ZnCl.$$

On mixing chloride of acetyl with oxybenzamate of zinc, sufficient heat is given off to volatilize a considerable part of the chloride of acetyl, if care be not taken to condense it, and the whole quickly solidifies to a hard mass (probably a combination of the two substances, analogous to the combination of hydrochloric acid with oxybenzamic acid), which, in a sealed tube at 100°, melts, and then again gradually solidifies; complete solidification indicates the end of the reaction.

Oxybenzamate of zinc heated with two equivalents of acetic acid, or a mixture of equivalent quantities of hydrochlorate of oxybenzamic acid and acetate of calcium with a little acetic acid, yields the same product; but neither of these processes is advantageous, on account of the high temperature required, and the difficulty of thoroughly mixing the materials.

* $C = 12$, $O = 16$.

† Oxybenzamate of zinc is easily obtained by mixing solutions of chloride of zinc and oxybenzamate of calcium. It separates as a granular precipitate which is very easily washed on a filter. It is nearly insoluble in water, but soluble in acetic acid.

·3624 grm., dried at 100°, was boiled with carbonate of sodium till completely decomposed: the resulting carbonate of zinc yielded on ignition ·0921 grm. oxide of zinc.

	Calculated.	Found.
Zinc per cent.	21·16	20·42

I have found the formation of this salt to be a convenient method of separating oxybenzamic acid from impure solutions.

The substance yielded by these reactions is easily purified. It is sufficient to dissolve it in an alkali, to precipitate the solution by hydrochloric acid, and to crystallize the precipitate two or three times from boiling water or alcohol. Any colouring matter which still adheres to the product thus obtained may be completely removed by animal charcoal.

I have named the new substance *acetoxybenzamic acid.*

Dried over sulphuric acid, it does not lose weight at 100°.

·3788 grm., prepared from acetic and oxybenzamic acids, gave ·8382 grm. carbonic acid, and ·1766 grm. water.

·2913 grm., prepared from chloride of acetyl and oxybenzamate of zinc, gave ·6396 grm. carbonic acid, and ·139 grm. water.

·4363 grm. of another similar preparation gave ·9677 grm. carbonic acid, and ·1987 grm. water.

·4302 grm. of the same product, heated with soda-lime, gave a platinum-salt containing ·2375 grm. platinum.*

·4442 grm. of the same product gave 29·2 cc. nitrogen at 0° and 760 mm. pressure.

		Calculated.	Found.					
								Mean.
C_9	108	60·33	60·36	59·88	60·49	—	—	60·24
H_9	9	5·03	5·18	5·23	5·06	—	—	5·16
N	14	7·82	—	—	—	7·80	8·25	8·02
O_3	48	26·82	—	—	—	—	—	26·64
$C_9H_9NO_3$	179	100·00						100·00

Acetoxybenzamic acid is obtained as a white powder, which, under the microscope, is seen to be formed of needle-shaped crystals. It is almost insoluble in cold water and in ether, and is only moderately soluble in boiling water or in cold alcohol; in boiling alcohol it dissolves easily. It has a slightly bitter taste, a good deal resembling that of nitre. Like its isomer hippuric acid, it dissolves readily in a solution of common phosphate of sodium, giving an acid reaction to the liquid, but is reprecipitated by acetic or a mineral acid. It is soluble in strong sulphuric acid without colouration in the cold, and also in glacial acetic acid; these solutions are precipitated by dilution with water. A mixture of

* In the decomposition of acetoxybenzamic acid by soda-lime very little ammonia is formed; nearly the whole of the nitrogen is given off as aniline.

acetoxybenzamic acid with sufficient strong hydrochloric or nitric acid to make it flow easily becomes nearly solid on standing for a few minutes, but it was found that a mixture of hydrochloric acid and acetoxybenzamic acid loses all its hydrochloric acid when dried under a bell-jar over lime and sulphuric acid.

At about 200° acetoxybenzamic acid sublimes somewhat rapidly; it melts between 220° and 230°, and enters into ebullition at about 260°, apparently undergoing decomposition at the same time. It may be boiled for a long time with water, and even with dilute acids, without undergoing perceptible change; but when heated in a sealed tube with hydrochloric or dilute sulphuric acid to about 140° it is decomposed into oxybenzamic and acetic acids, just as hippuric acid is decomposed under similar circumstances into glycocol and benzoic acid. A quantity of hydrochlorate of oxybenzamic acid thus obtained, gave the following results on analysis: —

·3767 grm., burned with chromate of lead, gave ·677 grm. carbonic acid, and ·1719 grm. water.

·1399 grm. gave ·3624 grm. chloride of silver.

	Calculated.	Found.
Carbon	48·42	49·01
Hydrogen . . .	4·61	5·07
Chlorine	20·46	20·39

Another quantity of acetoxybenzamic acid was decomposed by dilute sulphuric acid of 10 per cent. When the decomposition was complete, the contents of the tube were transferred to a retort and distilled. The distillate was saturated with carbonate of barium, filtered, and evaporated. The barium-salt so obtained proved to be acetate of barium.

·8039 grm., dried at 120°, gave ·7345 grm. sulphate of barium.

	Calculated. $C_2H_3BaO_2$	Found.
Barium per cent.	53·73	53·72

The residue in the retort deposited, on cooling, crystals of sulphate of oxybenzamic acid.

Acetoxybenzámic acid is similarly decomposed by an alcoholic solution of hydrochloric acid, but oxybenzamate and acetate of ethyl are formed at the same time as the corresponding acids. The

decomposition takes place slowly in the cold, but quickly at 100°. On distilling the product of the reaction in a water-bath, a light ethereal liquid, possessing the smell and general properties of acetate of ethyl, passed over with the excess of alcohol, and was separated from it by the addition of water. The residue in the retort crystallized on cooling in radiating needles. The crystals, which were very soluble in water and alcohol, but slightly soluble in ether, were recrystallized from water, washed with ether, and dried over sulphuric acid.

·4718 grm. gave ·3501 grm. chloride of silver.
·392 grm. gave ·2924 grm. chloride of silver.
·5091 grm., burned with chromate of lead, gave ·9642 grm. carbonic acid, and ·2638 grm. water.

These results correspond to a mixture of the hydrochlorates of oxybenzamic acid and oxybenzamate of ethyl.

	Hydrochlorate of oxybenzamic acid.	Found.		Hydrochlorate of oxybenzamate of ethyl.
Carbon . . .	48·42	51·65		53·60
Hydrogen . .	4·61	5·76		5·96
Chlorine . . .	20·64	18·24	18·15	17·62

What was left of the crystals, after making the above analyses, was dissolved in water, a slight excess of milk of lime added, and the whole shaken up with ether. The ether left, on evaporation, an oily liquid, apparently oxybenzamate of ethyl, which was nearly insoluble in water, but soluble in hydrochloric acid, giving a chloride insoluble in ether and combining readily with bichloride of platinum. The quantity of the platinum salt obtained was not sufficient for a determination of the percentage of platinum. The aqueous liquid, from which the ether had been poured off, was filtered, and the excess of lime separated by carbonic acid. After being somewhat concentrated by evaporation, it gave with chloride of zinc a precipitate resembling oxybenzamate of zinc.

Attempts were made to obtain acetoxybenzoic acid, $C_9H_8O_4$, isomeric with benzoglycollic acid, by the action of nitric oxide on a mixture of nitric acid and acetoxybenzamic acid, and also by the action of nitrous acid on a boiling aqueous solution of acetoxybenzamic acid, but in both cases the only product was a nitro-substitution compound.

Acetoxybenzamate of potassium was prepared by digesting a

solution of the acid in strong alcohol with dry carbonate of potassium. It is exceedingly soluble in water, and dissolves easily in alcohol, but is precipitated from this solution by ether. From a solution in alcohol containing more than about 10 per cent. of water, it is precipitated by ether in the form of a strong aqueous solution which solidifies only after standing for a considerable time.

Acetoxybenzamate of sodium, $C_9H_8NaNO_3 + xH_2O$.—This salt was prepared in the same way as the potassium salt. It is very soluble in water and easily soluble in alcohol, but can be obtained crystallized somewhat more easily than the potassium salt. It is insoluble in ether, and is not deliquescent.

·468 grm., dried between 120° and 130°, gave ·1636 grm. sulphate of sodium.

	Calculated. $C_9H_8NaNO_3$	Found.
Sodium per cent. . .	11·44	11·32

Acetoxybenzamate of barium, $C_9H_8BaNO_3 + 1\frac{1}{2}H_2O$.—Obtained by saturating a hot aqueous solution of the acid with carbonate of barium. It is very soluble in water and crystallizes by the spontaneous evaporation of its solution in minute radiating needles grouped together in tufts. It dissolves readily in spirit of wine, but is precipitated from a strong aqueous solution by absolute alcohol. It loses only a part of its water of crystallization at 100°; for analysis it was dried between 130° and 145°.

1·8854 grm., dried over sulphuric acid, lost ·1812 grm. water between 130° and 145°.
·8776 grm. lost ·0887 grm. water at the same temperature.
·6164 grm. of the dry salt gave ·3027 grm. sulphate of barium.
·3783 grm. gave ·1774 grm. sulphate of barium.
·3918 grm. gave ·1824 grm. sulphate of barium.
·9185 grm., burned with chromate of lead, gave 1·4625 grm. carbonic acid, and ·288 grm. water.

	Calculated.		Found.			
C_9	108	43·81	—	—	—	43·43
H_8	8	3·25	—	—	—	3·48
Ba	68·5	27·79	27·54	27·32	27·42	—
N	14	5·68	—	—	—	—
O_3	48	19·47	—	—	—	—
$C_9H_8BaNO_3$	246·5	100·00				

	Calculated.	Found.	
	$C_9H_8BaNO_3 + 1\frac{1}{2}H_2O$		
Water of crystallization . .	9·87	9·61	10·11

Acetoxybenzamate of calcium, $C_9H_8CaNO_3 + 1\frac{1}{2}H_2O$.—This salt was prepared by saturating the acid with milk of lime and removing the excess of lime by carbonic acid. It is only moderately soluble in cold water, and can be easily obtained in well-defined crystals, consisting of very thin rhombic plates, by cooling its hot aqueous solution.

·6428 grm., air-dry, lost ·081 grm. water at 130°.
·63 grm. lost ·0781 grm. water at 130°.
·2978 grm., dried at 130°, gave ·1039 grm. sulphate of calcium.
·2087 grm. gave ·0722 grm. sulphate of calcium.
·312 grm., burned with chromate of lead, gave ·6786 grm. carbonic acid, and ·1337 grm. water.

		Calculated.	Found.		
C_9	108	54·55	—	—	54·12
H_8	8	4·04	—	—	4·34
Ca	20	10·10	10·26	10·17	—
N	14	7·07	—	—	—
O_3	48	24·24	—	—	—
$C_9H_8CaNO_3$	198	100·00			

	Calculated.	Found.	
	$C_9H_8CaNO_3 + 1\frac{1}{2}H_2O$		
Water of crystallization . . .	12·0	12·6	12·4

Acetate of *lead* gives, with a solution of an acetoxybenzamate, a sticky precipitate which melts in boiling water and gradually dissolves; it is also soluble in alcohol.

Nitrate of *silver* and chloride of *zinc*, give no precipitate with a moderately strong solution of an acetoxybenzamate. With a concentrated solution, nitrate of silver gives a precipitate which blackens on boiling.

Acetoxybenzamate of ethyl.—This substance cannot be obtained by the process indicated by Stenhouse for the preparation of hippurate of ethyl, namely, by heating the acid with alcohol saturated with hydrochloric acid. The manner in which acetoxybenzamic acid is decomposed under these circumstances has already been described. When acetoxybenzamic acid and absolute

alcohol are heated together, no apparent action takes place at 100°; but at about 150° a compound is formed which is soluble in ether and can thus be separated from the acid which remains in excess. This body, which is probably acetoxybenzamate of ethyl, is very slightly soluble in cold water, but tolerably soluble in hot water; from this solution it sometimes separates, by cooling, in the form of an oil which solidifies gradually on standing. If long boiled with water it regenerates acetoxybenzamic acid. It is very soluble in alcohol. On heating this substance to 100° in a Liebig's drying-tube, in order to dry it for analysis, a few drops of a colourless liquid which was scarcely soluble in water but miscible with alcohol, and which greatly resembled carbolic acid in taste and smell, condensed in the tube leading to the aspirator. As this liquid continued slowly to distil after the substance had been heated for many hours to 100°, the temperature was raised to between 130° and 135°. At this temperature the liquid distilled more rapidly and was accompanied by a crystalline sublimate; at the same time the supposed acetoxybenzamate of ethyl rapidly became of a dark brown colour. Neither the liquid nor the sublimate was obtained in sufficient quantity for further examination.

Cahours* mentions a substance which he obtained by the action of chloride of benzoyl on oxybenzamate of silver, but of which he neither gives the formula nor describes the properties. Hoping to obtain benzoyl-oxybenzamic acid, I reacted on oxybenzamate of zinc with chloride of benzoyl. The product was an acid insoluble in cold water and in ether, slightly soluble in boiling water, in alcohol, and in chloroform, and resembling acetoxybenzamic acid in taste and in its appearance under the microscope. A determination of nitrogen by Dumas's process and the mean of two concordant combustions gave the following results:—

Carbon	68·03
Hydrogen	5·12
Nitrogen	6·27
Oxygen	20·58
	100·00

which differ too much from the calculated composition of benzoyl-oxybenzamic acid; namely—

* Ann. Ch. Pharm., ciii. 90. This product is spoken of as glycobenzamic acid in the Handwörterbuch.

Carbon	69·71
Hydrogen	4·56
Nitrogen	5·81
Oxygen	19·92
	100·00

It is a matter of some interest to consider the relation in which acetoxybenzamic acid stands to hippuric acid, and the nature of the isomerism of these two bodies.

If we bear in mind the close analogy which exists between glycocol and oxybenzamic acid, the formation of acetoxybenzamic acid from chloride of acetyl and oxybenzamate of zinc is strictly comparable to the formation of hippuric acid from chloride of benzoyl and zinc-glycocol; and its decomposition, when heated with water in presence of a strong acid, into acetic and oxybenzamic acids is analogous to the decomposition of hippuric acid into benzoic acid and glycocol.

C_2H_3OCl	+	$C_7H_6ZnNO_2$	=	$C_9H_9N_3O$	+	$ZnCl$
Chloride of acetyl.		Oxybenzamate of zinc.		Acetoxybenzamic acid.		
C_7H_5OCl	+	$C_2H_4ZnNO_2$	=	$C_9H_9NO_3$	+	$ZnCl$
Chloride of benzoyl.		Zinc-glycocol.		Hippuric acid.		

$C_9H_9NO_3$	+	H_2O	=	$C_2H_4O_2$	+	$C_7H_7NO_2$
Acetoxybenzamic acid.				Acetic acid.		Oxybenzamic acid.
$C_9H_9NO_3$	+	H_2O	=	$C_7H_6O_2$	+	$C_2H_5NO_2$
Hippuric acid.				Benzoic acid.		Glycocol.

Allowing for the difference between acetyl and benzoyl, acetoxybenzamic acid is to oxybenzamic acid what hippuric acid is to glycocol. The simplest way of expressing these relations in the formulæ of the two substances is to write acetoxybenzamic acid as an acetyl-derivative of oxybenzamic acid (or as oxybenzamic acid in which an atom of hydrogen is replaced by acetyl), and hippuric acid as a benzoyl-derivative of glycocol (or as glycocol in which an atom of hydrogen is replaced by benzoyl).

Before we can give formulæ which will indicate the further relations of these acids, it is therefore necessary to consider the formulæ of glycocol and oxybenzamic acid. These two bodies occupy corresponding positions in two analogous series of compounds.

Acetic acid .	$C_2H_4O_2$	Benzoic acid .	$C_7H_6O_2$
Chloracetic acid	$C_2H_3ClO_2$	Nitrobenzoic acid	$C_7H_5(NO_2)O_2$
Glycocol . .	$C_2H_5NO_2$	Oxybenzamic acid	$C_7H_7NO_2$
Glycollic acid	$C_2H_4O_3$	Oxybenzoic acid	$C_7H_6O_3$

There are two principal points of view from which the members of the two series may be regarded, and accordingly two principal systems of rational formulæ by which they may be represented. We may, on the one hand, adopt formulæ expressing only the genetic relations of the two sets of compounds to acetic and benzoic acids respectively; or, on the other hand, formulæ which express in addition the general nature of the differences which the various terms of each series exhibit in their relation to other substances. In the first case, if we write acetic and benzoic acids as deriving from the type H_2O, we get—

Acetic Series.

Acetic acid . . . . $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$

Chloracetic acid . . . $\left.\begin{matrix}C_2H_2ClO\\H\end{matrix}\right\}O$

Glycocol. . . . . $\left.\begin{matrix}C_2H_2(H_2N)\\H\end{matrix}\right\}O$

Glycollic acid . . . . $\left.\begin{matrix}C_2H_2(HO)\\H\end{matrix}\right\}O$

Benzoic Series.

Benzoic acid . . . . $\left.\begin{matrix}C_7H_5O\\H\end{matrix}\right\}O$

Nitrobenzoic acid . . . $\left.\begin{matrix}C_7H_4(NO_2)O\\H\end{matrix}\right\}O$

Oxybenzamic acid . . . $\left.\begin{matrix}C_7H_4(H_2N)O\\H\end{matrix}\right\}O$

Oxybenzoic acid . . . $\left.\begin{matrix}C_7H_4(HO)O\\H\end{matrix}\right\}O$

In the second case we get the following, or equivalent formulæ:—

Acetic Series.

			Type.
Acetic acid . . .	$\left.\begin{array}{r} H \\ C_2H_2O \end{array}\right\}$ $\left.\begin{array}{r} C_2H_2O \\ H \end{array}\right\} O$	. .	$\left.\begin{array}{r} H \\ H \end{array}\right\}$ $\left.\begin{array}{r} H \\ H \end{array}\right\} O$
Chloracetic acid . .	$\left.\begin{array}{r} Cl \\ C_2H_2O \end{array}\right\}$ $\left.\begin{array}{r} C_2H_2O \\ H \end{array}\right\} O$	. .	$\left.\begin{array}{r} Cl \\ H \end{array}\right\}$ $\left.\begin{array}{r} H \\ H \end{array}\right\} O$
Glycocol	$\left.\begin{array}{r} H \\ H \\ C_2H_2O \end{array}\right\} N$ $\left.\begin{array}{r} C_2H_2O \\ H \end{array}\right\} O$	. .	$\left.\begin{array}{r} H \\ H \\ H \end{array}\right\} N$ $\left.\begin{array}{r} H \\ H \end{array}\right\} O$
Glycollic acid . . .	$\left.\begin{array}{r} H \\ C_2H_2O \end{array}\right\} O$ $\left.\begin{array}{r} C_2H_2O \\ H \end{array}\right\} O$	. .	$\left.\begin{array}{r} H \\ H \end{array}\right\} O$ $\left.\begin{array}{r} H \\ H \end{array}\right\} O$

Benzoic Series.

Benzoic acid . . .	$\left.\begin{array}{r} H \\ C_7H_4O \end{array}\right\}$ $\left.\begin{array}{r} C_7H_4O \\ H \end{array}\right\} O$	. .	$\left.\begin{array}{r} H \\ H \end{array}\right\}$ $\left.\begin{array}{r} H \\ H \end{array}\right\} O$
Nitrobenzoic acid . .	$\left.\begin{array}{r} NO_2 \\ C_7H_4O \end{array}\right\}$ $\left.\begin{array}{r} C_7H_4O \\ H \end{array}\right\} O$	. .	$\left.\begin{array}{r} NO_2 \\ H \end{array}\right\}$ $\left.\begin{array}{r} H \\ H \end{array}\right\} O$
Oxybenzamic acid . .	$\left.\begin{array}{r} H \\ H \\ C_7H_4O \end{array}\right\} N$ $\left.\begin{array}{r} C_7H_4O \\ H \end{array}\right\} O$	. .	$\left.\begin{array}{r} H \\ H \\ H \end{array}\right\} N$ $\left.\begin{array}{r} H \\ H \end{array}\right\} O$
Oxybenzoic acid . .	$\left.\begin{array}{r} H \\ C_7H_4O \end{array}\right\} O$ $\left.\begin{array}{r} C_7H_4O \\ H \end{array}\right\} O$	. .	$\left.\begin{array}{r} H \\ H \end{array}\right\} O$ $\left.\begin{array}{r} H \\ H \end{array}\right\} O$

It will be seen that these two systems of formulæ differ in this: that, in the first set, the type remains unchanged throughout, but that the radicle is different in each compound; while, in the

second set, the type is variable but the radicle constant. It may perhaps be said that this difference is not essential, but merely a difference of form: the elements which, in the one case, are represented as replacing hydrogen in the radicles acetyl and benzoyl and are written in the same line with the remaining elements of these radicles, being, in the other case, separated and written above the other elements. Admitting this to be the case, and supposing the two sets of formulæ to be used in the same sense, the question arises whether or no one set of formulæ is preferable to the other as a matter of form.

On this point it may be observed, first, that the only consistent definition of a compound radicle is *a group of elements contained in a greater or less number of substances and not altered by the reactions by which these substances are transformed one into another*, and that it is therefore inconsistent to represent closely allied and mutually convertible substances as containing different radicles; secondly, that the only consistent use of typical formulæ is *to express the nature of the transformations which the bodies represented by them are capable of undergoing*, and, therefore, that it is inconsistent to refer to the same type, bodies of which the transformations are very different. For example, the formulæ—

$$\left.\begin{matrix} C_7H_5O \\ H \end{matrix}\right\} O \qquad \left.\begin{matrix} C_7H_4(NO_2)O \\ H \end{matrix}\right\} O \qquad \left.\begin{matrix} C_7H_4(H_2N)O \\ H \end{matrix}\right\} O$$

Benzoic acid, Nitrobenzamic acid, Oxybenzamic acid,

ought to imply that the salts of these three acids give similar products when acted upon by acid chlorides, such as chloride of acetyl or chloride of benzoyl: experiment, however, proves that the first two give anhydrides when so acted upon, while the third gives a well characterized acid. The same difference also exists between the salts of acetic acid and the salts of glycocol in respect to their behaviour with similar reagents.

For these reasons, the relations of glycocol and oxybenzamic acid to their congeners are most correctly expressed by the formulæ—

$$\begin{matrix} \left.\begin{matrix} H \\ H \\ C_2H_2O \end{matrix}\right\} N \\ \left.\begin{matrix} \\ H \end{matrix}\right\} O \end{matrix} \qquad \text{and} \qquad \begin{matrix} \left.\begin{matrix} H \\ H \\ C_7H_4O \end{matrix}\right\} N \\ \left.\begin{matrix} \\ H \end{matrix}\right\} O \end{matrix}$$

Glycocol. Oxybenzamic acid.

which represent them as amidic acids corresponding respectively to

glycollic (oxyacetic) acid and oxybenzoic acid. Hence, for hippuric and acetoxybenzamic acids we get the formulæ—

$$\left.\begin{matrix} H \\ C_7H_5O \end{matrix}\right\} N \qquad\qquad \left.\begin{matrix} H \\ C_2H_3O \end{matrix}\right\} N$$
$$\left.\begin{matrix} (C_2H_2O)'' \\ H \end{matrix}\right\} O \quad \text{and} \quad \left.\begin{matrix} (C_7H_4O)'' \\ H \end{matrix}\right\} O$$

Hippuric acid. (Benzoyl-oxyacetamic acid.) Acetyl-oxybenzamic acid.

By way of justification of this discussion of what may seem very obvious formulæ, I may perhaps be allowed to give a collection (probably far from complete) of formulæ which have recently been proposed for glycocöl, hippuric acid, and oxybenzamic acid.

Glycocol.	Hippuric acid.	Oxybenzamic acid.
$N\left\{\begin{matrix} C_2H_3O_2 \\ H \\ H \end{matrix}\right.$	$N\left\{\begin{matrix} C_2H_3O_2 \\ C_7H_5O \\ H \end{matrix}\right.$	

Gerhardt, Traité iv, 767, (1

$C_4H_3(H_2N)O_4$		$C_{14}H_5(H_2N)O_4$

Cahours, Ann. Ch. Phys., [3] liii, (1

$N\left\{\begin{matrix} \left.\left\{\begin{matrix} C_2H_2'O \\ H \end{matrix}\right.\right\} O \\ H_2 \end{matrix}\right.$		$N\left\{\begin{matrix} \left.\left\{\begin{matrix} C_7H_4O \\ H \end{matrix}\right.\right\} O \\ H_2 \end{matrix}\right.$

Wislicenus, Zeitschr. f. d. gesammt. Naturwissenschaften, xiv, (1

$N\left.\left\{\begin{matrix} C_2HO_2 \\ C_2H_3 \\ H \end{matrix}\right.\right\} O_2$ *	$N\left.\left\{\begin{matrix} C_2\ \overset{''}{O}_2 \\ C_{14}H_5O_2 \\ C_2\ H_3 \\ H \end{matrix}\right.\right\} O_2$ *	$\overset{''}{N}\left.\left\{\begin{matrix} C_{14}H_5O_2 \\ H_2 \end{matrix}\right.\right\} O_2$ *

Weltzien, Zusammenstell. d. organ. Verbind. (1

$\left.\begin{matrix} C_4\overset{\frown}{H_2(N}H_2')O_2 \\ H \end{matrix}\right\} O_2$ *	$\left.\begin{matrix} C_{14}H_4.(C_4\overset{\frown}{H_2.N}H_2.O_2)O_2 \\ H \end{matrix}\right\} O_2$ *	$\left.\begin{matrix} C_{14}\overset{\frown}{H_4(N}H_2)O_2 \\ H \end{matrix}\right\} O_2$ *

Gorup-Besanez, Lehrb. d. organ. Chemie, ii, (1

$HO.\left(C_2\left\{\begin{matrix} H_2 \\ H_2N \end{matrix}\right.\right)[C_2O_2].O$ *	$HO.C_{12}\left\{\begin{matrix} H_4 \\ \left(C_2\left\{\begin{matrix} H_2 \\ H_2N \end{matrix}\right.\right) C_2O_2 \end{matrix}\right\}[C_2O_2].O$ *	$HO.\left(C_{12}\left\{\begin{matrix} H_4 \\ H_2N \end{matrix}\right.\right)[C_2O$

Kolbe, Ann. Ch. Pharm., cxiii, (1

$\left.\begin{matrix} H \\ H \\ CO \end{matrix}\right\} N$ $\left.\begin{matrix} CH_2 \\ H \end{matrix}\right\} O$	$\left.\begin{matrix} H \\ C_7H_5O \\ C'O \end{matrix}\right\} N$ $\left.\begin{matrix} C\ H_2 \\ H \end{matrix}\right\} O$	

Limpricht, Lehrb. d. organ. Chemie, (1

* In the formulæ marked with an asterisk, H = 1, C = 6, O = 8.

It is hardly necessary to add, in conclusion, that I make no claim to originality in reference to the formulæ proposed in this paper. Gerhardt, in the formula quoted above, represented hippuric acid as benzoyl-glycocol, and the formulæ which I have adopted for oxybenzamic acid and glycocol were first proposed by Kekulé (Ann. Ch. Pharm., civ. 148; cvi. 150). Moreover, the formulæ for glycocol and hippuric acid which are quoted from Limpricht are very nearly identical with those proposed in this paper. The only difference is, that in order to represent other reactions than those which are here taken into account, he has divided the radicle C_2H_2O into CO and CH_2, and has consequently derived glycocol and hippuric acid from the type $\left.\begin{matrix} H_5N \\ H_2O \end{matrix}\right\}$, which might perhaps be more correctly written $\left.\begin{matrix} H_2 \\ H_3N \\ H_2O \end{matrix}\right\}$; for though in some compounds nitrogen is combined with the equivalent of five atoms of hydrogen, these substances are always easily broken up into a group equivalent to H_2 and a group equivalent to H_3N.

Through the kindness of Professor Kekulé, of the University of Ghent, I have been able to perform the experiments described in this paper in his laboratory.

Ghent, 19th June, 1860.

XXI.—*On Baudrimont's Protosulphide of Carbon.*

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Baudrimont has given various processes for the preparation of protosulphide of carbon, a body long expected by chemists and necessary to complete the analogy between sulphur and oxygen. Protosulphide of carbon bears the same analogy to carbonic oxide that bisulphide of carbon does to carbonic acid. The discovery of the body surprised no one, but it was a matter of astonishment that the numerous and simple processes for its preparation had remained so long unknown to chemists.

The description given by Baudrimont* for the preparation and properties of this interesting body is short, further details being promised in a future paper. Meanwhile, the new compound has received admission into systematic works on Chemistry.

Being desirous of making some experiments with protosulphide of carbon, I have repeated without success the processes described by Baudrimont; I have been equally unsuccessful with others which appeared equally promising. It is therefore desirable to obtain further evidence of this existence of the compound; for the products of the processes described are in most cases only carbonic oxide with the vapours of bisulphide of carbon, and, in other cases, mixtures of carbonic oxide, hydrogen, carburetted hydrogen and the vapours of bisulphide of carbon.

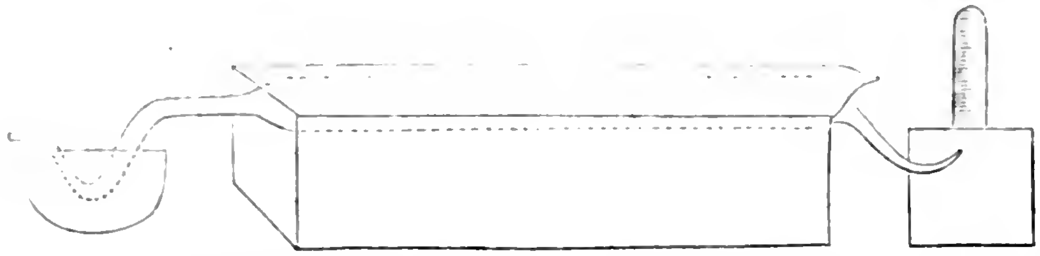
Baudrimont, in the memoir above referred to, gives nine processes for the preparation of protosulphide of carbon, but admits that only the first process yielded it in a state of tolerable purity. To this process it will therefore be sufficient to direct special attention. The vapours of bisulphide of carbon are to be passed over red hot pumice-stone or spongy platinum, which have the effect, according to Baudrimont, of doubling the compound, (so much sulphur being at the same time deposited as to choke the exit tubes), while the gaseous protosulphide of carbon passes on, and may be collected, after transmission through solutions of acetate of lead and dichloride of copper.

In repeating this and subsequent experiments, it became obvious that the presence of organic matter and moisture was a frequent source of error, and it was necessary to operate so as to exclude these; accordingly the following arrangement was adopted:—

A long tube of difficultly fusible glass was filled with fragments of pumice-stone to the extent of three feet in length, and then the posterior end was drawn out into a U shape, and the anterior end into a delivery tube for gaseous products. The capacity of the whole tube was about 95 cubic centimeters. The body of the tube containing the pumice stone was placed in Hofmann's gas furnace and heated, a stream of carbonic acid, dried by sulphuric acid, being passed over it until all moisture was expelled. When the desiccation of the tube and pumice-stone had been effected, 8 grammes of dry bisulphide of carbon were sucked into the U portion of the tube, which was then sealed by a lamp and placed in a water-bath.

* Comptes rendus, xliv, 1000.

The whole of the bisulphide of carbon was now slowly passed over the red hot pumice and the products were collected over mercury by the delivery portion of the tube. The heat employed was sufficient to alter the shape of the tube, although it was protected as is usual in combustion, by metallic gauze.



During the experiment gas came over, and with it liquid bisulphide which condensed in the eudiometer. After the 8 grammes of bisulphide had been slowly passed over the red hot pumice-stone, the products were as follows :—

Gas at 730mm. press. 12°C. temp. . . .	155 cub. cent.
Liquid bisulphide of carbon	5 cub. cent.

The gas corrected for temp. and pressure, and for the tension of CS_2 with which it was saturated (200mm. at 12°C. Brezelius) gave

Corrected vol. of gas and 0°C. and 760mm. press. 103·5 cub. cent.

Caustic potash was now passed up to absorb carbonic acid and sulphuretted hydrogen, and the gas now measured 59 cub. cent. at 12°C. and 610mm. pressure, still saturated with bisulphide of carbon. Corrected for this and brought to the normal temperature and pressure there was only 30·49 cub. cent. of gas left.

Hence of the 8 grammes of bisulphide, at least 6·4 grammes were found condensed in the eudiometer; the remaining 1·6 gramme was chiefly in the long delivery tube, which had a column of condensed bisulphide in it, but this was not measured. If we neglect this and assume that 1·3 gramme was decomposed into protosulphide of carbon (0·3 gramme in vapour being allowed for the capacity of the tube), 383 cub. cent. of this gas should have been produced. But after correcting for the pressure, temperature, and for the tension of CS_2, only 30·49 cub. cent. were obtained. This small quantity of residual gas consisted of carbonic oxide and nitrogen, resulting from the traces of air and moisture still left in the pumice-stone, or introduced when the bisulphide of carbon was drawn into the apparatus. But if we assumed the whole residual gas to be protosulphide of carbon, it would have

weighed only 0·060 gramme, and would have been produced from 0·09 gramme of the bisulphide. Hence in any case not more than 1·4 per cent. of the bisulphide employed could have been decomposed in its passage through the red-hot pumice. But this gas was chiefly carbonic oxide produced by the action of moisture—($CS_2 + HO = CO + S + HS$,) and required only 0·027 HO to produce it, a quantity which can easily have escaped the drying process.

A careful examination of the tube and pumice-stone showed that no sulphur whatever was deposited, except one or two specks which could not have been weighed, the whole operation having been one of simple distillation without decomposition. When the pumice-stone is not completely dry, then sulphuretted hydrogen and carbonic oxide appear, while sulphur is deposited.

Having failed in obtaining protosulphide of carbon by the only process which Baudrimont describes as giving it pure, it was scarcely necessary to repeat the other methods; but those described as yielding the best results were examined. The chief of these is to pass the vapours of bisulphide of carbon over red-hot charcoal, animal charcoal being recommended.

On repeating these experiments, large quantities of gas were obtained at first; but the gas ceased abruptly, although the tube still contained abundance of animal charcoal, and now bisulphide of carbon distilled over unchanged. The gas collected in the first part of the experiment was washed with solution of acetate of lead and dichloride of copper, but continually decreased in bulk, until only a small quantity remained. This was analysed with the following results:—20·295 cub. cent. gave

Carbonic oxide	11·79
Bisulphide of carbon . . .	4·66
Nitrogen	3·83
	20·28

The analysis was however only approximate, as some sulphuric acid was formed in the combustion of the gas.

A like experiment made with wood-charcoal gave precisely similar results.

Both these experiments proved that the gas at first obtained was due to the organic matter and moisture acting on the bisulphide of carbon and that the latter distilled over unchanged, as soon as the former were removed.

It is unnecessary to describe the other experiments made in the hope of procuring protosulphide of carbon, as they all gave negative results.

Baudrimont gives as evidence of the compositon of the gas obtained by him (1) that lime-water decomposed it into sulphide of calcium and its own volume of carbonic oxide. It is clear that this experiment was not a quantitative one, as no allowance is made for the solubility of the protosulphide of carbon, which is stated to dissolve in its own bulk of water. Hence the result may have been due to a mere mixture of carbonic oxide containing the vapour of bisulphide of carbon and a little sulphuretted hydrogen. (2) Baudrimont states that eudiometric analysis gave equal volumes of CO_2 and SO_2; but this result would be equally attained by the combustion of a gas containing equal volumes of CS_2 and CO; and, at the ordinary temperature, with the diminished pressure in the eudiometer, the tension of CS_2 is more than sufficient to double the volume of gas in the tube. It may further be remarked that Baudrimont does not give any process for removing bisulphide of carbon from the gases obtained by him.

In conclusion, it must be admitted that there is no sufficient evidence of the existence of protosulphide of carbon, all the processes described for its preparation having failed to yield it. Buff and Hofmann* seem to have been equally unsuccessful in their endeavours to obtain it from bisulphide of carbon by electric incandescence.

XXII.—*Notice of a New Ammonio-Chrome Compound.*

By J. Morland, F.C.S.

When sulphocyanide of ammonium is fused, and powdered bichromate of potash added to it, this salt dissolves quietly at first, giving a purple coloration. After a short time, however, a very brisk reaction ensues, ammonia and aqueous vapour are given off abundantly, and the residue is of a beautiful crimson colour. This residue consists of sulphocyanide of ammonium, sulphocyanide of potassium, bichromate of potash, sulphate of potash and the sulphocyanide of a new ammonio-chrome com-

* Journal of Chemical Society, xii, 283.

pound; this last salt is easily purified from the others by washing with cold water, in which it is but sparingly soluble, and afterwards by crystallization from alcohol, which dissolves it freely, or from ether, in which it is moderately soluble. This new salt has the composition, $Cr_2 \; Csy_3 \; 2NH_4O$. Analysis gave the following figures:—

	Theory.	Found.	
Cr	18·71	18·71	when the salt was dried at 120° C
S	34·53	34·37	
N	25·18	24·96	
C	12·95	13·27	
H	2·88	3·39	
O	5·76		

This is a perfectly neutral salt, crystallizing in the cubical system. I obtained crystals by the spontaneous evaporation of an ethereal solution, the form of which was the rhombic dodecahedron modified by the planes of the octahedron: it has a strongly bitter taste, especially at the back of the mouth. Heated in a closed tube, it gives off ammoniacal vapours, sulphuretted hydrogen, and some compound of cyanogen with a garlicky odour; the residue is sulphide of chromium, which, when heated in the air, ignites, gives off sulphurous acid, and leaves sesquioxide of chromium.

Neither acids nor alkalies decompose this salt in the cold, but alkalies on boiling throw down oxide of chrome; and acids, when concentrated, decompose it by uniting with the ammonia. Heated on the water-bath with sulphuric acid, it yields sulphate of ammonia and blue sulphate of chrome; oxalic acid gave violet oxalate of chrome and oxalate of ammonia.

Persalts of iron are not coloured by this salt, but nitrate of silver immediately gives a precipitate of uncertain composition, as much of this chrome salt is carried down.

Other chromates as well as bichromate of potash also form this same salt with fused sulphocyanide of ammonium; chromate of potash, and chromate of lead succeed pretty well, but there are also other substances formed. I found the best proportion to be 5 of sulphocyanide to 2 of bichromate, corresponding to 1 eq. bichromate to 5 of sulphocyanide.

Frémy's roseo-chrome salts have the composition

$$(Cr_2O_3.4NH_3).3A,$$

which differs chiefly in the double quantity of ammonia. The cobalt-bases have, according to Frémy, the following compositions :—

$$Co_2O_3 \; 4 \; NH_3$$
$$,, \quad 5 \quad ,,$$
$$,, \quad 6 \quad ,,$$

I have attempted to form other compounds by the reduction of chromates in the presence of ammonia-salts, but at present without success.

XXIII.—*On Circular Polarization.*

A Discourse delivered to the Members of the Chemical Society of London.

By Dr. J. H. Gladstone, F.R.S.

When, at the request of the Council, I undertook to bring the subject of circular polarization before the Chemical Society, I did not realize the quantity of the observations which have been recently accumulated by the industry of foreign *savans.* In preparing this discourse, I have been well-nigh overwhelmed with materials, and I have therefore considered it best to omit all description of the more purely physical questions, and to confine myself as closely as possible to those branches of the subject which have a direct bearing on chemical science.

Circular polarization was first observed in quartz by Arago, in 1811; it was investigated by Biot,* and the subject speedily attracted the attention of some of the leading physicists of this country. Brewster, Herschel, and Airy made important discoveries in respect to it; but since that early period, very little has been done by the scientific men of Great Britain, while in France and other parts of the continent, investigations have rapidly extended, and circular polarization has been taken advantage of for the solution of many chemical problems. It is true, that soon after the formation of our Society, Leeson read an elaborate

* Mem. Inst. 1812, and subsequently.

communication on the subject;* some of Pasteur's papers have been translated in our Quarterly Journal,† and the matter has of course been referred to in lectures and treaties on Natural Philosophy;‡ yet there can be no doubt that British Chemists have generally made themselves but little acquainted with the subject.

The leading phenomena of circular polarization are simply these. If a slice be cut from a crystal, endowed with this property, in a direction perpendicular to its axis, and it be examined by polarized light, it does not exhibit the coloured rings and black cross; and if the emergent polarized ray be analysed by a doubly-refracting prism, the two images have complementary colours, which change as the prism is made to revolve. If such a slice of crystal, or a liquid possessing the same power, be placed between the polarizer and analyser of a polariscope, the maximum and minimum of light are in fact not attained when the plane of reflection is inclined to that of polarization at 0° and 90°, but at some other angles 90° apart. The amount of this deflection will differ with the colour—that is, with the refrangibility of the ray; thus a violet ray will be deflected to perhaps twice the distance of a red ray; and hence when white light is employed, a series of colours are observed following one another in regular succession, as the analyser is made to revolve. If, in order to make these follow in their natural order—red, orange, yellow, green, blue, violet—it is necessary to turn the analyser to the right—that is to say, in the direction of the hands of a watch—the substance is said to exhibit right-handed or positive circular polarization, which is usually indicated by the sign or + : if, on the contrary, the analyser must be turned to the left to produce the same result, the polarization is left-handed, or negative, and the sign or — is employed. On revolving the analyser beyond the violet rays, the same order of colours, beginning with red, reappears, and there is a transition tint, called by the French *teint de passage* or *teint sensible,* which from its sensitiveness is very valuable for observations.

* Mem. and Proc. Chem. Soc., ii, 26.

† Chem. Soc. Qu. J., iii, 79; v, 62; vi, 273, 277.

‡ For instance, in Golding Bird's Elements of Natural Philosophy; in Pereira's Lectures, Pharm. J., ii and iii; in Graham's Elements of Chemistry, 2nd Edit., Vol. ii, p. 464; and in a lecture by Maskelyne, Phil. Mag. (4), i, 428.

For the explanation of these phenomena on the undulating theory, I can only refer to Fresnel's Memoirs.*

Substances which exhibit Circular Polarization.—The following table contains a list of the substances in which the phenomena of circular polarization have been observed. It is doubtless incomplete; and it must be borne in mind also that the effects are produced by very many compounds of some of these bodies, which are not included in the table. Against the name of the substance is placed the sign + or −, to indicate the direction of the rotation, and in another column the name of the observer who first remarked the property in the substance in question, or who has worked upon it to the greatest effect. Where a second observer has discovered the existence of a power of rotation in a direction opposite to that first discovered, which is by no means an uncommon circumstance, or has otherwise largely extended our knowledge of the subject, his name has generally been added. The last column indicates whether the substance has been observed to form hemihedral crystals, either itself or in its compounds.

Substance.	Direction.	Authority.	Hemihedral?
Quartz crystal	+ or −	Arago, Biot, Brewster, Herschel	Hem.
Chlorate of soda (solid)..	+ or −	Marbach	Hem.
Bromate of soda (solid)..	+ or −	,,	
Acetate of uranium and soda (solid) ..	+ or −	,,	
Cinnabar..	+ or −	Descloizeaux	
Oil of turpentine ..	+ or −	Biot, Seebeck, Leeson	
Oil of lemon	+	,,	
Oil of bergamotte ..	+	,,	
Oil of anise	−	,,	
Oil of carraway	+	,,	
Oil of spearmint ..	−	,,	
Oil of rue	−	,,	
Oil of nutmeg	+	Leeson	
Oil of lavender	−	,,	
Oil of cubebs	−	Wilhelmy	
Oil of valerian	−	,,	
Oil of amber	−	,,	
Castor oil	+	,,	
Croton oil	+	,,	
Balsam of copaiba ..	−	,,	
Camphor..	+ or −	Biot, Chantard	

* Ann. Ch. Phys. (2), xxviii, 147. This is abstracted in Daguin's *Traité Elémentaire de Physique*, which contains many of the most recent observations on the subject.

Substances.	Direction.	Authority.	Hemi-hedral?
Camphoric acid	+ or −	Bouchardat, Chautard	Hem.
Camphoethylic acid ..	+	Malaguti	Hem.
Camphomethylic acid ..	+	Loir	Hem.
Naphtha	−	Biot	
Cane-sugar	+	,, Clerget	Hem.
Milk-sugar ..	+	,, Poggiale	Hem.
Grape-sugar	−	,,	
Starch-sugar	+	,, Béchamp	
Diabetes-sugar		,, Clerget, Listing	
Glucosate of sea-salt ..	+	Pasteur	Hem.
Tartaric acid	+ or −	Biot, Pasteur, Arndtzen	Hem.
Malic acid	+	Pasteur	Hem.
Tartramide	+ or −	,,	Hem.
Asparagine	−	,,	Hem.
Tartramic acid	+ or −	,,	Hem.
Aspartic acid	+	,,	
Sulphamylic acid ..		,,	Not
Amylic alcohol		,,	
Formobenzoic acid ..			
Quinic acid			Hem.
Quinine	−	Bouchardat, Pasteur	
Quinidine	+	,, ,,	
Quinicine	+	Pasteur	
Cinchonine	+	Bouchardat	
Cinchonidine	−	Pasteur	
Cinchonicine	+	,,	
Quinoidine	+	Wilhelmy	
Morphine	−	Bouchardat, Pasteur	Hem.
Brucine	−	,,	
Strychnine	−	,, Descloizeaux	
Narcotine	+	,,	
Nicotine	−	Wilhelmy	
Santonine	−	,,	
Hœmatoxylin	+	,,	
Jalapin	−	,,	
Phloridzin	−	,,	
Salicin	−	Bouchardat, Biot and Pasteur	
Populin	−	Biot and Pasteur	
Codeine	−	Bouchardat and Boudet	
Narceine	−	,, ,,	
Picrotoxine	−	,, ,,	
Albumin	+	A. Becquerel	

I have not attempted to express in this table the amount of rotatory force possessed by the different substances, not from any lack of numerical data, but for the following reasons:—

1st. It has been frequently determined differently by different observers. This arises to some extent from actual optical differences in the samples employed: thus oil of turpentine is known to possess different powers of rotation, even when the direction remains the same, according to the kind of pine from which it

came, and the processes adopted in preparing and purifying it. Again, the amount of solvent employed is a fruitful cause of diversity.

2nd. Unfortunately, in determining the rotatory force, no uniform standard has been adopted. Thus, Biot reduces his observations to a unit of thickness—namely, one millimeter, and he calculates from the arc of rotation of the rays that have passed through red glass. He employs the following formula for determining the specific rotatory power (ρ), in which a stands for the arc of rotation, d the density, and l the thickness or length in millimeters.

$$\rho = \frac{a}{d\,l}$$

And if the substance be dissolved in some optically neutral solvent, the proportion of the said substance in one part of the solution (p) has to be taken into account, and the formula stands—

$$\rho = \frac{a}{d\,l\,p}$$

Wilhelmy,* on the contrary, laying stress on the molecular nature of the force, considers it preferable to take the different substances in quantities proportional to their atomic weights in equal weights of the solvent; and where he cannot do this, he makes a reduction on the hypothesis that the relative quantity of the solvent has no influence. He makes his calculations also for white light, and assumes the molecular rotating power of cane sugar as 100.

A table given in one of Wilhelmy's papers† is so good an illustration of the elaborate investigations that have been made into this subject, that I have reproduced it here.

Substance.	Quantity dissolved	Solvent.	Degree of rotation. White Light.	Degree of rotation. Red Light.	Atomic weight. O = 100.	Molecular rotating power. (White light.)
	millgr.					
Cane-sugar	4309	Water	+ 32°·5	+ 25°	2154·5	+ 100
Nicotine	1301	Alcohol	– 16			
—— with hydrochloric acid	,,	,,	+ 1(?)			
Santonin	500	,,	– 9	+ 6·7	3005	– 332·3
Hematoxylin	1849	,,	..	+ 13·5		
Jalapin	2000	,,	..	– 7		

* Pogg. Ann., lxxxi, 413, 499.

† Ibid, lxxxi, 527.

Substance	Quantity dissolved	Solvent	Degree of rotation. White Light.	Red Light.	Atomic weight O = 100.	Molecular rotating power. (White light.)
	milligr.		°	°		
Camphor	6000	Alcohol	+31	+22	963·8	+30·7
Phloridzin	2377	,,	−11	−8·7	2082·5	−59·2
Quinine	1782	,,	−24	−20	2055·5	−174
——	891	,,	−12·5	−9·65		
—— with nitric acid ..	,,	,,	−17	..	..	−241·4
—— with phosphoric acid	,,	,,	−15	..	..	−213
Sulphate of quinine ..	1000	Water & sulp. acid	−24·5	−16·7		
Valerate of quinine ..	..	Alcohol	−16	−13		
Hydrochlorate of quinine ..	500	,,	−10			
Cinchonine	454	,,	+12	..	1942	+315·8
—— with oxalic acid ..	494	,,	+12·5	..	..	+302
—— with phosphoric acid	952	,,	+23·5	..	..	+295
—— with nitric acid ..	930	,,	+20	..	..	+257
—— ,, ,, ..	465	,,	+10			
Quinoidine	374	,,	+9·5	+8		
—— with nitric acid ..	,,	,,	+9·75			
—— with phosphoric acid ..	,,	,,	+10			
—— with hydrochloric acid	,,	,,	+10			
—— with sulphuric acid ..	,,	,,	+11·5			
Brucine	984	,,	−8	..	3448	−172·5
—— with phosphoric acid	,,	,,	0			
Narcotine with sulphuric acid	936	Water	+5·5	..	4684	+169
Acetate of morphine ..	490	,,	−4			
Hydrochlorate of codeine ..	578	,,	−5			
Ethereal oil of cubebs ..	7460	Alcohol	+33·5			
—— ,, valerian ..	7480	Ether	−15·4			
Balsam of copaiva	7560	Ether with alch.	−11·5			

Influence of state of Aggregation.—The only substance which has been examined in the three different states of aggregation—the solid, liquid, and gaseous, is oil of turpentine, and it has been found to exhibit the power in each of these states. It rotates the plane of polarization to the same extent when frozen as when in its ordinary liquid condition; but Biot, who made the experiment on the vapour of turpentine, was unable to determine whether the power was then altered in amount. It was necessary, as will be readily understood, to look through a large amount of the vapour in order to observe any effect on polarized light; in fact, an iron tube 15 metres, that is 50 feet, long was employed for the experiment, and unfortunately before the quantitative determination was completed, a burst of flame occurred, and gave rise to

a conflagration which the philosopher could not extinguish without the assistance of the public.

Yet, while oil of turpentine is so retentive of this power, its very existence in some other substances appears to depend on the manner in which they are crystallized. Thus silica does not show any effect on polarized light as it exists in the opal, or indeed in any other form than that of quartz-crystal.

Influence of temperature.—Just as the refrangibility of a substance changes with alterations of the temperature, and that not *pari passu* with the change of density, so also the amount of rotatory power varies under like circumstances. There are however great differences between one substance and another in this respect.

Quartz shows an increased power of rotating the plane of polarization when it is heated, and that to the extent of 108° or 109·5° for an elevation of 70° C. of temperature. This crystal is known to expand by heat differently in the direction transverse to what it does in that parallel to its axis.

Tartaric acid is similarly affected, and that to such an extent that Biot found himself able, by reducing the temperature, actually to reverse the direction of the rotation in solid amorphous tartaric acid, the right-handed deviation diminishing, becoming *nil*, and the left-handed commencing before the thermometer sank to 3° C.

Grape-sugar in solution is much effected by changes of temperature; and in saccharimetry by means of polarized light, account must be taken of this circumstance. Clerget,* who has studied this subject, finds that the power of rotation decreases—not increases—as the temperature rises, and that according to the quantity of sugar, quite irrespective of the proportion of water; indeed, it is the same whether 100 parts of water dissolve 1 or 120 parts of sugar. He found the decrease between 10° C. and 35° C. to be in the proportion of very nearly 100 to 91. Wilhelmy has determined it for a much longer range of temperature, and deduced the formula

$$D' = D\ [1 - 0{\cdot}012\ (t' - t)]$$

in which D and D′ represents two amounts of rotation corresponding with the temperatures t and t'.

* Ann. Ch. Phys., [3] xxvi, 175.

Salts of quinine, and many other substances, are also known to vary in their power of rotating a ray of polarized light according to the temperature.

Yet, on the other hand, it is stated that the essential oil of turpentine has exactly the same power at 55° C. as at 10° C., and even when frozen.

Influence of Magnetism or Electricity.—I cannot help alluding to the beautiful discovery of Faraday, that a polarized ray passing through optically inactive bodies may be caused to rotate by the magnetic or electric force, and that the rotation in active bodies, such as oil of turpentine, may be altered, or even reversed, at will. This part of the subject, however, I must not pursue further, as it belongs purely to the domain of physics.

Influence of Solution.—Substances which exhibit circular polarization are affected by solution in three different manners.

1st. There are substances, as chlorate of soda, bromate of soda, and the double acetate of uranic oxide and soda, the crystals of which exhibit evidences of circular polarization, but are perfectly inactive when dissolved in water.* These bodies, like quartz, appear to owe this property to the manner in which their molecules are arranged in the crystals.

2nd. There are other substances, all of them organic, which exhibit the same polarizing power, whether they are in the solid state or dissolved in some optically neutral solvent, such as water or alcohol. This cannot generally be determined, as in most crystals of such bodies the phenomena of circular polarization are masked by the double refraction; but "barley-sugar" has been found to have the same or nearly the same power of rotation as the sugar when dissolved in water; and it has been recently shown that, whatever the amount of water in which it is dissolved, the rotatory power of sugar is rigorously constant.† Oil of turpentine belongs to this class. In such cases, the substances seem to owe their power of rotating the plane of polarization to the very structure of their molecules.

3rd. There are other substances in which the result partakes to

* Marbach, Ann. Ch. Phys, [3] xliii, 252, xliv, 41. Biot confirms and draw philosophical deductions from these experiments.

† Arndtzen, Ann. Ch. Phys., [31] iv, 403.

a certain extent of both these characters, where, indeed, it would seem that the individual action of the molecules is accompanied in the solid state by another action arising from their regular arrangement. Thus sulphate of strychnine* evaporated at a temperature of between 10° C. and 20° C. gives a salt which contains 13 atoms of water. It crystallizes in the system of the rectangular prism with a square base, and is of such a form as to allow the recognition of the circularly polarizing power. It rotates the ray, in fact, to about half the extent that left-handed quartz does; but the solution of sulphate of strychnine in water, though it also rotates the plane, does so only to $\frac{1}{24}$th or $\frac{1}{25}$th part of the extent to which these crystals do.

Tartaric acid when obtained in a transparent, solid, amorphous state by mixing it with boracic acid, was found to exhibit circular polarization; but different proportions of water cause very remarkable, and as yet unexplained, differences in the optical character of a solution of tartaric acid. The plane of polarization of the green rays is in fact caused to deviate more than that of any other colour, and Arndtzen, who has worked out the whole of this matter with much care and ability, found when operating with ordinary (that is right-handed) tartaric acid dissolved in alcohol instead of water, that he could obtain a left-handed rotation for the blue rays. The same observer found, in reference to camphor dissolved in alcohol, that the rotatory power augments with the refrangibility of the rays more rapidly than in the case of most active bodies, and that the rotatory power decreases regularly with the concentration of the solution.†

Influence of Chemical Combination or Substitution.—In most cases this property appears to be so intimately connected with the structure of the molecule itself, that it is unaffected, or little affected, by chemical changes of an important character.

Thus an optically active acid, such as tartaric acid, will carry its rotatory power into its salts; and similarly an optically active base, such as quinine, will exhibit the phenomena of circular polarization when combined with inactive acids. From observations on neutral and bitartrate of potash and ammonia, which are isomorphous, Pasteur‡ has drawn the conclusion that when

* Descloizeaux, Ann. Ch. Phys., [3] li, 361.

† Ann. Ch. Phys., [3] liv, 403. Biot had experimented on these matters previously; see Ann. Ch. Phys., [3] xxxvi, 257, 405.

‡ Inst., 1850, 339.

quantities of isomorphous substances corresponding to the equivalents are dissolved in equal quantities of water, these solutions rotate the plane of polarization to an equal degree. But it must not be supposed that as a general rule the optically inactive base or acid exerts no modifying influence on the phenomena exhibited by the active element with which it is combined. A glance at the above quoted table of Wilhelmy will show that it is otherwise. Bouchardat* has given numbers which indicate that the combination of camphoric acid with soda or with ammonia reduces its rotatory power; some malates have a positive, others a negative rotation; and, as a further example, asparagine if dissolved in pure water or in alkalis turns the plane of polarization to the left, but if in mineral acids, it turns it to the right.†

Oxidation even does not necessarily destroy this power, for camphor retains it when it has been oxidized into the camphoric acid just alluded to; nor does the substitution of a compound radicle for hydrogen, as is shown by the optical properties of camphovinic‡ and camphomethylic acids.§ The conversion of an acid into an amide, and that again into the corresponding amidogen-acid, is not even fatal to the retention of this optical power, as is evidenced by the activity not only of tartaric acid, but also of tartramide and tartramic acid; and, in a parallel manner not only of malic acid, but also of malamide and malamic acid—that is, asparagine and aspartic acid.‖

It must, however, be supposed in reference to every circularly polarizing substance, that there is some amount of chemical change which the molecule cannot suffer without losing this property. In the case of the two acids just mentioned, tartaric and malic, we find this point passed, when by the action of heat they are converted into other acids, with evolution of part of their constituent elements: for pyrotartaric, fumaric, and maleic acids have no effect on the polarized beam.¶ And here must be mentioned one of Pasteur's remarkable observations. From fumarate of ammonia, which is inactive, aspartic acid may be produced; but this, unlike ordinary aspartic acid, is itself inactive; and again from this may be reproduced malic acid, which also in its turn, unlike

* Comp. rend., xxviii, 319. † Pasteur, Ann. Ch. Phys. [3] xxxi, 67.
‡ Malaguti. § Loir, Ann. Ch. Phys., [3] xxxviii, 483.
‖ Pasteur, Ann. Ch. Phys. [3] xxxviii, 437. ¶ Ibid, xxxi, 67.

that derived directly from the plant, has no influence on the polarized beam.*

As yet we have no evidence that an optically active substance has ever been artificially prepared from one that is optically inactive, though such is constantly occurring in nature. The tartaric acid which Liebig has very recently prepared has been found to rotate the plane of polarization like natural tartaric acid,† but then it must be borne in mind that it was prepared from milk-sugar, which is itself endowed with this property. It will be interesting to determine whether the tartaric acid which Perkin and Duppa have just succeeded in preparing from succinic acid exhibits this power, for succinic acid as yet is not classed among those bodies which display it. Yet from its analogy to tartaric and malic acids, it would appear highly probable that succinic acid should rotate the polarized beam. A specimen said to have been prepared from stearic acid was found by me to be perfectly inactive; but it is quite possible that the succinic acid prepared from malic acid, or that which Dessaignes‡ announces he has prepared from tartaric acid, may prove capable of rotating a ray of light.

The mutual relationship of the substances here referred to will be readily understood by a reference to the following table:

	C = 6; O = 8	C = 12; O = 16
Tartaric acid . .	$2HO.C_8H_4O_{10}$	$C_4H_6O_6$
Malic acid . .	$2HO.C_8H_4O_8$	$C_4H_6O_5$
Succinic acid . .	$2HO.C_8H_4O_6$	$C_4H_6O_4$
Tartramide . .	$C_8H_8N_2O_8$	$C_4H_8N_2O_4$
Asparagine . .	$C_8H_8N_2O_6$	$C_4H_8N_2O_3$
Tartramic acid .	$HO.C_8H_6NO_9$	$C_4H_7NO_5$
Aspartic acid . .	$HO.C_8H_6NO_7$	$C_4H_7NO_4$
Pyrotartaric acid .	$HO.C_6H_3O_5$	$C_3H_4O_3$
Fumaric acid . .	$2HO.C_8H_2O_6$	$C_4H_4O_4$
Maleic acid . .	$2HO.C_8H_2O_6$	$C_4H_4O_4$

Relation between Crystalline Form and the power of Circular Polarization.—As far back as 1820 Herschel found that the crystals of right-handed and of left-handed quartz differ in form, and from the inclination of certain facets he was able to foretel

* Ann. Ch. Phys., [3] xxxiv, 30. † Bohn, Ann. Ch. Pharm., Jan. 1860.
‡ Compt. rend., April 16, 1860.

what would be the direction of the rotation in any particular specimen;* but it was reserved for Pasteur to show that this relation between the crystalline form and the rotatory power is one that generally obtains.

It is well known that the law of symmetry does not hold good in all crystals. These exceptional forms have been termed hemihedral. It will sometimes happen also that a substance will crystallize in two forms which are both unsymmetrical, but unsymmetrical in opposite directions—that is to say, the one form will appear identical with the other only when it is seen reflected in a mirror. They differ, in fact, in the same way as one side of our face differs from the other, or as our two hands differ. These are variously called not superposable, incongruous, or opposite hemihedra.

From an observation of the opposite hemihedral character of crystals of the double racemate of soda and ammonia, Pasteur commenced that series of observations which led him to the discovery that racemic acid is composed of two tartaric acids, with opposite but equal powers of polarization, conjoined together as one substance; to the isolation of left-handed tartaric acid; to the artificial preparation of racemic acid; and of a neutral and unresolvable tartaric acid†—discoveries which, however interesting, I refrain from dwelling on, as the papers in which they are explained have been printed in our Quarterly Journal, and are well known to chemists in this country.

The same philosopher has shown by a great number of instances that when a substance crystallizes in opposite hemihedra, it indicates the existence of two opposite powers of rotation, and that active and inactive bodies will not crystallize together, however isomeric.‡ Yet it cannot be laid down as a universal law that this property of matter in a crystalline state is always accompanied with the power of circular polarization, for formate of strontia gives opposite hemihedra, but neither kind of crystal when separated from the other and dissolved, has any influence on polarized light.§ Sulphate of magnesia is an analogous instance. Nor, on the other hand, can it be affirmed that this

* See his remarks on this subject in his article on Light in the Encyc. Metrop., par. 1042, in which he almost prophecies more recent discoveries.

† Ann. Ch. Phys., [3] xxiv, 442: xxviii, 56, and Compt. rend., xxxvii, 162.

‡ Ann. Ch. Phys. [3] xxxviii, 437.

§ Ibid, xxxi, 67.

optical property is necessarily connected with the power of forming such crystals; for two sulphamylic acids have been discovered which are isomeric, and absolutely identical in the crystalline form of their salts, without showing any disposition to form hemihedra, and yet the one is active and the other inactive.*

The inactive aspartic acid derived from fumarate of ammonia does not crystallize in hemihedra, as the ordinary aspartic acid does; and similarly there are some differences in the crystalline forms of the salts of the natural or active, and of the artificial or inactive malic acid.

Marbach† has observed that though chlorate of soda crystallizes in opposite hemihedra, and in that condition exercises an influence on the polarized beam, yet a solution of either right-handed or left-handed crystals alone is perfectly inactive, and the salt crystallizes out from such a solution in *both* forms instead of that only from which it was made.

Circular Polarization as applied to Chemical Inquiries.

The phenomena of circular polarization have been applied to many practical purposes in chemical research. These may be conveniently grouped under three heads—the quantitative estimation of certain organic products; the determination of what is going forward in a solution; and the examination of isomeric substances.

1st. *Quantitative estimation of certain organic products.*

Cane Sugar.—As cane sugar dissolved in water rotates the ray of polarized light to an extent directly proportional to the amount of sugar in a given depth of liquid, and irrespective of the amount of water, or of the simultaneous presence of optically inactive substances, this property is frequently made use of to effect a quantitative determination. Clerget‡ has worked out this process very fully, and others§ have since somewhat extended or modified his observations. Instruments have been devised for

* Compt. rend., xlii, 1259.

† Ann. Ch. Phys., [3] xliv, 41.

‡ Ibid. xxvi, 175.

§ Especially Wilhelmy and Arndtzen, in papers previously referred to; Pohl, Wien. Acad. Bericht, xxi, 492; and Michäelis, Journ. Pharm. Chem., lxxv, 464.

the purpose by Biot, Soleil,* Savart, Powell,† Leeson,‡ Mitscherlich, but the simplest, and perhaps the most effective, is a modification of Biot's apparatus which Mr. Heisch employs, and has kindly lent me on this occasion. It consists essentially of three parts—a polarizer, an analyser, and a tube for holding the solution. The polarizer is a Nicoll's prism and plano-convex lens to render the rays parallel; the analyser consists of a small aperture in a brass plate, a lens, and an achromatic prism of doubly refracting spar, and it is attached to the vernier of a graduated circle. The tube through which the polarized beam passes between the polarizer and the analyser is a narrow tube of black glass ground in the inside with coarse emery, and fitted at each end with covers of perfectly parallel glass. Several such tubes of various known lengths, so as to hold different quantities of liquid are provided, and the position of the polarizer and analyser can be easily adapted to each. If when the index of the scale is at 0°, and the extraordinary image is at its greatest obscuration, a solution of sugar be placed in the tube, it is easy to determine how much the analyser must be now turned round in order to bring the extraordinary image again to its greatest obscuration, or rather to the "sensitive tint." It is impossible here to enter into the minutiæ of the apparatus, or of the treatment of the solution; suffice it to say that Heisch prefers operating by lamp light, and has found that it requires 6·09 per cent. of cane-sugar to produce a rotation of 1° in a depth of 1 inch: hence the percentage in the solution examined may be reckoned according to the simple formula

$$p = 6{\cdot}09 \frac{a}{l}$$

a representing the arc of rotation, and l the length in inches.

An ingenious method of confirming the amount of cane-sugar in a solution, or of determining it in the presence of other optically active bodies, is founded on the property possessed by this sugar of being converted by acids into a sugar which exhibits the opposite or left-handed rotation. The following

* The English reader will find a description of this instrument by Dr. Bence Jones in the Pharm. Journ. and Trans., xi, 455.

† Phil. Mag., April, 1843.

‡ Mem. Chem. Soc., ii, 26.

formula serves for this inverted sugar, according to Heisch, at 15° C.

$$p \quad = \quad 16{\cdot}026\,\frac{a}{l}$$

As glucose rotates the plane of polarization to the right, and is not capable of inversion by acids, this process will even serve to determine the respective amounts of cane-sugar and glucose if mixed together in solution. Or the same may be effected by determining the rotation of the mixed solution, boiling it with potash, which destroys the glucose, and then again determining the rotation which is now due solely to cane-sugar.

Other sugars.—Bence Jones* has published analyses of the different wines of commerce, in which he determined the grape-sugar by means of Soleil's saccharimeter.

Poggiale† has employed a similar method for the estimation of the amount of sugar in milk.

Listing‡ has published optical determinations of the sugar in diabetic urine. The formula of Heisch for this sugar is

$$p \quad = \quad 8{\cdot}346\,\frac{a}{l}$$

If albumin be present, it must be removed, as it possesses itself an influence on polarized light.

Albumin.—This substance may likewise be estimated by means of its rotating power, and A. Becquerel§ has in fact measured in this way the proportion of albumin contained in the serum of blood.

2nd. *Determination of what is going forward in a solution.* The variations in the plane of polarization will often indicate changes in a solution which could not be watched by any other method, or even the existence of which might never otherwise have been recognized.

Thus Wilhelmy‖ investigated the action of sulphuric, phosphoric, nitric, and hydrochloric acids on cane-sugar, and examined mathematically the progress of the change with reference to time. He satisfied himself that the final result of the conversion of the sugar is independent of the quantity of acid originally added.

* Proc. Roy. Inst. Vol. i. † Compt. rend., xxviii, 505, 584.
‡ Ann. Ch. Pharm., xcvi, 93, 101. § Compt. rend., xxix, 625.
‖ Pogg. Ann. lxxxi, 413, 499.

Biot investigated a very curious state of combination between tartaric acid and boracic acid when they are both dissolved together in water, and he endeavoured to determine the nature of the transformation which tartaric acid undergoes when acted on by heat. He has applied circular polarization also more widely to the study of the question of the condition of a substance in solution. The papers* which contain these inquiries are very lengthy, and include much philosophical reflection on the subject in general.

Thus also, from some observations of Bouchardat on the effect of polarized light on camphoric acid, the same saturated with soda, and then supersaturated with hydrochloric acid, I was able to derive from a novel source an additional illustration of the reciprocal decomposition of binary compounds in solution.†

Béchamp‡ too, from observations with the polariscope, arrived at the conclusion that crystallized starch sugar is a combination which cannot exist indefinitely except in the solid state, and that when dissolved in water it loses its combined water, slowly in the cold, but rapidly under the influence of heat, resembling in this respect hydrated oxide of copper or hydrated oxide of iron in the presence of water. In fact he supposes that the $C_{12}H_{12}O_{12}.2HO$ when dissolved passes, during the lapse of a certain number of hours, wholly into $C_{12}H_{12}O_{12}$.

3rd. *Examination of isomeric substances.*

Reference has already been made to the researches of Pasteur by which he unravelled the relations between racemic and tartaric acids, and enriched our knowledge of many organic compounds by exhibiting isomeric bodies identical with them save in their action on polarized light, and perhaps their crystalline form. Their solubility appears also in some instances to be slightly affected. His discoveries however have not been confined to those already alluded to. Finding that there exist two sulphamylic acids, the one possessed of the rotatory power and the other not possessing it, he was able by their decomposition to produce two amylic alcohols differing slightly in their physical properties.§ His very original examination of the cinchona

* Ann. Ch. Phys., xxviii, 215, 351; xxxvi, 257, 405.

† Chem. Soc. Qu. J., ix, 148.

‡ Compt. rend., xlii, 640. Dubrunfaut differs from this explanation, *ibid,* 739; but Béchamp defends his own view, *ibid,* 896.

§ Comp. rend., xlii, 1259.

alkaloids, and the two isomeric groups at the head of which stand quinine and cinchonine,* I shall only just refer to, as his paper was reproduced in our Quarterly Journal.†

Different isomeric essential oils of the composition C_5H_4 might be distinguished by this method, but the data seem wanting for the practical application of circular polarization to the analysis of them.

Berthelot‡ has by the same agency investigated a very remarkable change that takes place in oil of turpentine, or oil of lemons, by the action of acids, alkaline or earthy chlorides, or some other salts. This isomeric modification is indicated by a reduction of the rotatory power whether positive or negative; it never entirely disappears, but there are grounds for believing that the result is a mixture of unaltered oil, and oil which has been rendered inactive. It is not necessary that the salt which produces this singular change should dissolve in the oil, for even the insoluble fluoride of calcium has a strongly marked effect.

XXIV.—ON CHEMICAL ANALYSIS BY SPECTRUM-OBSERVATIONS.

By Professors KIRCHHOFF and BUNSEN.

(From Poggendorff's Annalen, Bd. cx. S. 161.)

It is well known that many substances possess the power of developing peculiar bright lines in the spectrum of a flame into which they are introduced. This property may be made the foundation of a method of qualitative analysis, which greatly enlarges the field of chemical reactions, and leads to the solution of problems hitherto unapproachable.

The bright lines produced in this manner, show themselves most plainly when the temperature of the flame is highest and its illuminating power least. Hence Bunsen's gas-burner, which gives a flame of very high temperature and very slight luminosity, is well adapted for experiments on the bright lines of the flame-spectra produced as above described.

The coloured plate at the end of this paper, shows the spectra given by such a flame when the chemically pure chlorides of potassium, sodium, lithium, strontium, calcium, and barium are

* Comp. rend , xxxvii, 110.

† Vol. vi, p. 273.

‡ Ann. Ch. Phys., [3] xxxviii, 38.

volatilised in it. The ordinary solar spectrum is added by way of comparison.

The potassium compound employed was obtained by igniting chlorate of potassium which had been previously recrystallized six or eight times. The chloride of sodium was prepared by neutralizing pure carbonate of sodium with hydrochloric acid and crystallizing the salt several times.

The salt of lithium was purified by precipitation fourteen times with carbonate of ammonium.

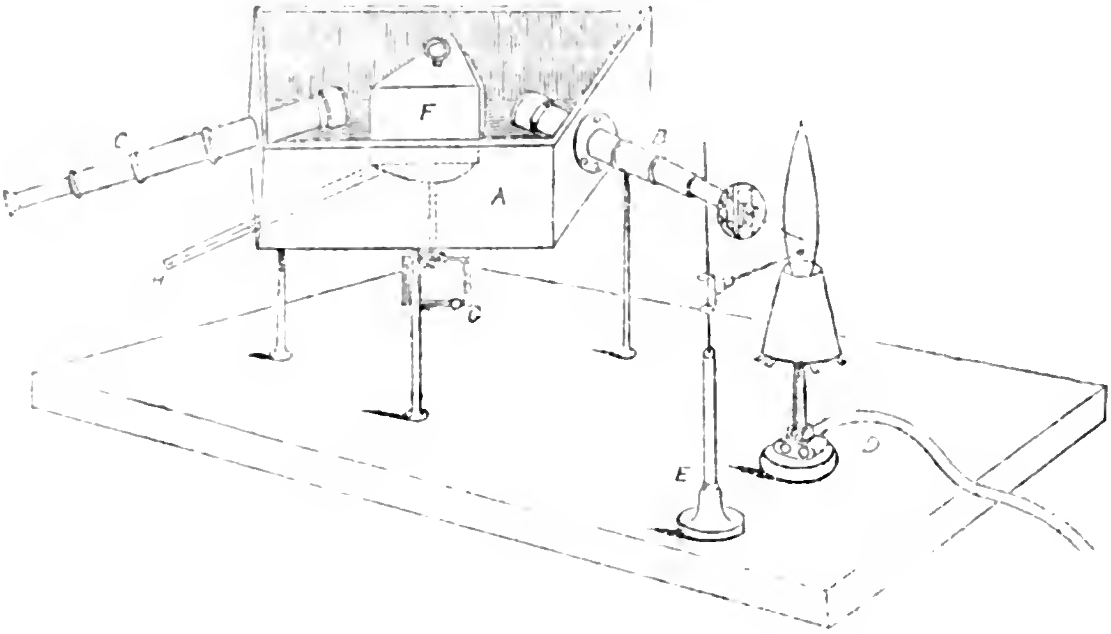
The purest specimen of marble which could be obtained, dissolved in hydrochloric acid, was the source of the calcium salt. From this solution the carbonate of calcium was thrown down in two portions by fractional precipitation with carbonate of ammonium, the latter half of the calcium salt being converted into the nitrate. The salt thus obtained was dissolved in absolute alcohol, and after evaporation of the alcohol, converted into the chloride by precipitation with carbonate of ammonium and solution in hydrochloric acid.

To obtain pure chloride of barium, the commercial salt was boiled out repeatedly with nearly absolute alcohol, and the residual salt freed from alcohol was dissolved in water, and thrown down by fractional precipitation in two portions. The second only of these portions was dissolved in hydrochloric acid, and the salt still further purified by repeated crystallizations.

Pure chloride of strontium was prepared by crystallizing the commercial salt several times from alcohol, and by fractional precipitation of the salt with carbonate of ammonium, the second portion being dissolved in nitric acid, and the nitrate freed from the last traces of calcium salt by boiling with alcohol. The product thus purified was lastly thrown down with carbonate of ammonium, and the precipitate dissolved in hydrochloric acid. All these various purifications were conducted as much as possible in platinum vessels.

The apparatus which we have usually employed for our spectrum-observations is represented in the annexed woodcut. A is a box blackened on the inside, having its horizontal section in the form of a trapezium, and resting on three feet; the two inclined sides of the box, which are placed at an angle of about 58° from each other, carry the two small telescopes B and C. The eye-piece of the first telescope is removed, and in its place is inserted a plate, in which a slit made by two brass knife-edges is so arranged that it coincides with the focus of the object-glass. The gas-lamp D stands before the slit in a position such that the mantle of the flame is in a straight line with the axis of the telescope B. Somewhat lower than the point at which the axis of the tube produced meets the mantle, the end of a fine platinum wire bent round to a hook is placed in the flame. The platinum wire is supported in

this position by a small holder, E, and on to the hook is melted a globule of the dried chloride which it is required to examine. Between the object-glasses of the telescopes B and C is placed a hollow prism, F, filled with bisulphide of carbon, and having a refracting angle of 60°. The prism rests upon a brass plate moveable about a vertical axis. The axis carries on its lower part the mirror G, and above that the arm H, which serves as a handle for



turning the prism and mirror. A small telescope placed some way off is directed towards the mirror, and through this telescope an image of a horizontal scale, fixed at some distance from the mirror, is observed. By turning the prism round, every colour of the spectrum may be made to move past the vertical wire of the telescope C, and any required position in the spectrum thus brought to coincide with this vertical line. Each particular portion of the spectrum thus corresponds to a certain point on the scale. If the luminosity of the spectrum is very small, the wire of the telescope C may be illuminated by means of a lens, which throws a portion of the rays from a lamp through a small opening in the side of the tube of the telescope C.

We have compared the spectra represented on the Plate, which were obtained from the pure chlorides, with those produced when the bromides, iodides, hydrates, sulphates and carbonates of the several metals are brought into the following flames:—

Into the flame of sulphur.
„ „ bisulphide of carbon.
„ „ aqueous alcohol.
Into the non-luminous flame of coal-gas.
Into the flame of carbonic oxide.
„ „ hydrogen.
Into the oxyhydrogen flame.

As the result of these somewhat lengthy experiments, the details of which we here omit, it appears that neither the alteration of

the bodies with which the several metals may be combined, nor the variety of the chemical processes occurring in the several flames, nor the wide differences of temperature which these flames exhibit, *produce any effect upon the position of the bright lines in the spectrum which are characteristic of each metal.*

The following considerations show how much the temperature of these various flames differ. An approximation to the temperature of a flame is obtained by help of the equation.

$$t = \frac{\Sigma gw}{\Sigma ps},$$

in which t signifies the required temperature of the flame, g the weight of one constituent of substance burning in oxygen, w the heat of combustion of this constituent, p the weight, and s the specific heat of one of the products of combustion. The heat of combustion of the following bodies may be taken as—

Sulphur	2240° C.
Bisulphide of carbon	3400
Hydrogen	34462
Marsh-gas	13063
Ethylene	11640
Butylene	11529
Carbonic oxide	2403

The specific heats under constant pressure were found by Regnault to be—

Sulphurous acid	= 0·1553
Carbonic acid	= 0·2164
Nitrogen	= 0·2440
Aqueous vapour	= 0·4750

Hence the temperatures of the flames are found to be—

The sulphur flame	1820° C.
The bisulphide of carbon flame	2195
The coal-gas flame*	2350
The carbonic oxide flame†	3042
The hydrogen flame in air‡	3259
The oxyhydrogen flame§	8061

It was found that the same metallic compound, placed in one of these flames, gives a more intense spectrum the higher the temperature of the flame. In the same flame, those compounds of a metal give the brightest spectra which are most volatile.

In order to prove still more conclusively that each of the above-mentioned metals always produces the same bright lines in the spectrum, we have compared the spectra represented in the Plate with those produced when the electric spark passes between electrodes made of these metals.

Small pieces of sodium, potassium, lithium, strontium, and calcium were fastened to fine platinum wires and melted two by

* Ann. Ch. Pharm. cxi. 258.
† Bunsen's 'Gasometry.' p. 242. ‡ Ibid. § Ibid.

two into glass tubes, so that the pieces of metal were separated by about 1 to 2 millims., and the platinum wires were melted through the sides of the glass tubes. Each of these tubes was placed in front of the spectrum-instrument, and by means of a Ruhmkorff's induction apparatus, sparks were allowed to pass between the pieces of metal inside the tube; the spectrum thus produced was then compared with that given by a gas-flame into which the chloride of the metal was brought. The flame was placed behind the glass tube. By alternately bringing the induction apparatus into and out of action, it was easy, without measuring, to convince ourselves that in the brilliant spectrum of the electric spark, the bright lines of the flame-spectrum were present in their normal position. Besides these lines, other bright ones appeared in the electric spark spectrum; some of these were produced by foreign metals present in the electrodes; others arose from nitrogen, which filled the tubes after the oxygen had combined with a portion of the electrodes.*

From these facts it appears certain that the appearance of the bright lines represented in the spectra on the Plate may be regarded as absolute proof of the presence of the particular metal. They serve as reactions by means of which these bodies may be recognized with more certainty, greater quickness, and in far smaller quantities than can be done by help of any other known analytical method.

The spectra drawn on the Plate represent those seen when the slit was of such a width that only the most conspicuous of the lines of the solar spectrum were visible, the magnifying power of the telescope C being a fourfold one, and the light of a moderate degree of intensity. These circumstances seem to us to be the most advantageous when it is required to make a chemical analysis by means of spectrum-observations. The appearance of the spectrum may, under other conditions, be essentially different. If the purity of the spectrum be increased, many of those lines which appeared before as single ones are split up into several; thus the sodium line is divided into two separate lines. If, on the other hand, the intensity of the light be increased, new lines appear in several of the spectra and the relative brightness of the old ones becomes altered. In general an indistinct line becomes brighter upon increasing the illumination, more rapidly than a brighter line, but not to such an extent that the indistinct line ever overtakes the brighter one in intensity. A good example of this is seen in the two lithium lines. We have observed only

* On employing on one occasion with strontium-electrodes a tube filled with hydrogen instead of nitrogen, the stream of sparks changed rapidly into a continuous arc of light, whilst a grey pellicle covered the inside of the tube. The tube was opened under rock-oil, when it was found to be empty, the hydrogen having disappeared. This gas appears, at the enormously high temperature of the electric spark, to have decomposed the oxide of strontium which was not completely removed from the metal.

one exception to this rule, namely in the line Ba η, which by light of small intensity is scarcely visible, whilst Ba γ appears plainly, but by light of greater intensity becomes more visible than the latter. We intend on a future occasion to examine this point in detail.

We now proceed to describe the peculiarities of the several spectra, the exact acquaintance with which is of practical importance, and to point out the advantages which this new method of chemical analysis possesses over the older processes.

Sodium.

The spectrum-reaction of sodium is the most delicate of all. The yellow line Na α, the only one which appears in the sodium spectrum, is coincident with Fraunhofer's dark line D, and is remarkable for its exactly defined form, and its extraordinary brightness. If the temperature of the flame be very high, and the quantity of the substance employed very large, traces of a continuous spectrum are seen in the immediate neighbourhood of the line. In this case too, the weaker lines produced by other bodies, when near the sodium line, are discerned with difficulty, and are often not seen till the sodium reaction has almost subsided.

The reaction is most visible in the sodium-salts of oxygen, chlorine, iodine, bromine, sulphuric acid, and carbonic acid; but it is always evident, even in the silicates, borates, phosphates, and other non-volatile salts.

Swan* has already remarked upon the small quantity of sodium necessary to produce the yellow line.

The following experiment shows that the chemist possesses no reaction which will bear the remotest comparison, as regards delicacy, with this spectrum-analytical determination of sodium. In a far corner of our experiment room, the capacity of which was about 60 cubic metres, we burnt a mixture of 3 milligrammes of chlorate of sodium with milk-sugar, whilst the non-luminous flame of the lamp was observed through the slit of the telescope. Within a few minutes, the flame, which gradually became pale yellow, gave a distinct sodium line, lasting for ten minutes, and then entirely disappearing. From the weight of sodium salt burnt, and the capacity of the room, it was easy to calculate that in one part by weight of air there was suspended less than $\frac{1}{20,000,000}$ of a part of soda-smoke. As the reaction can be quite easily observed in one second, and as in this time the quantity of air which is heated to ignition by the flame is found, from the rate of issue and from the composition of the gases of the flame, to be only about 50 cub. cent. or 0·0647 grm. of air, containing less than $\frac{1}{20,000,000}$ of sodium salt, it follows that the eye is able to detect

* Trans. Roy. Soc. Edinb. vol. xxi. Part III. p. 411.

with the greatest case quantities of sodium salt less than $\frac{1}{3,000,000}$ of a milligramme in weight. With a reaction so delicate, it is easy to understand why a sodium reaction is almost always noticed in ignited atmospheric air. More than two-thirds of the earth's surface is covered with a solution of chloride of sodium, fine particles of which are continually being carried into the air by the action of the waves. The particles of sea-water thus cast into the atmosphere, evaporate, leaving almost inconceivably small residues, which, floating about, are almost always present in the air, and are rendered evident to our eyesight in the sunbeam. These minute particles perhaps serve to supply the smaller organized bodies with the salts which larger animals and plants obtain from the ground; but there is also another point of view, in which the presence of this chloride of sodium in the air is of interest. If, as is scarcely doubtful at the present time, the explanation of the spread of contagious disease is to be sought for in some peculiar contact-action, it is possible that the presence of an antiseptic substance like chloride of sodium, even in almost infinitely small quantities, may not be without influence upon such occurrences in the atmosphere. By means of daily and long-continued spectrum observations, it would be easy to discover whether the alteration of intensity in the line Na *a* produced by the presence of sodium-compounds in the air, has any connection with the appearance and direction of march of an endemic disease.

The unexampled delicacy of the sodium reaction explains also the well-observed fact, that all bodies, after a lengthened exposure to air, show the sodium line when brought into a flame, and that it is only in a few salts that it is possible to get rid of the last traces of the line Na *a*, even after repeated crystallization from water which has only been in contact with platinum. A thin platinum wire, freed by ignition from every trace of sodium salt, shows the reaction most visibly after a few hours' exposure to the air. In the same way, the dust which settles from the air in a room, shows the bright line Na *a*: to render this evident it is only necessary to knock a dusty book, for instance, at a distance of some feet from the flame, when a wonderfully bright flash of the yellow band is seen.

Lithium.

The luminous ignited vapour of the lithium compounds gives two sharply defined lines, the one a very weak yellow line, Li *β*, and the other a bright red line, Li *a*. This reaction likewise exceeds in certainty and delicacy all ordinary methods of analytical research. It is, however, not quite so sensitive as the sodium reaction, only, perhaps, because the eye is more adapted to distinguish yellow than red rays. When 9 milligrammes of carbonate of lithium mixed with excess of milk-sugar were burnt, the reaction was visible in a room of 60 cubic metres capacity.

Hence, by the method already explained, we find that the eye is capable of distinguishing with absolute certainty a quantity of carbonate of lithium less than $\frac{9}{10,000,000}$ of a milligramme in weight: 0·05 grm. of carbonate of lithium salt, burnt in the same room, was sufficient to enable the ignited air to show the red line Li *a* for an hour after the combustion had taken place.

The compounds of lithium with oxygen, iodine, bromine, and chlorine are the most suitable for the purpose; still the carbonate, sulphate, and even the phosphate give almost as distinct a reaction. Minerals containing lithium, such as triphylline, triphane, petalite, lepidolite, require only to be held in the flame in order to obtain the bright line Li *a* in the most satisfactory manner. In this way the presence of lithium in many felspars can be directly shown, as, for instance, in the orthoclase from Baveno. The line is seen for a few moments only, directly after the mineral is brought into the flame. In the same way, the mica from Altenberg and Penig was found to contain lithium, whereas micas from Miask, Ashaffenburg, Modum, Bengal, Pennsylvania, &c., were found to be free from this metal. In natural silicates which contain only small traces of lithium, this metal is not observed so readily. The examination is then best conducted as follows:—A small portion of the substance is digested and evaporated with hydrofluoric acid or fluoride of ammonium, the residue moistened with sulphuric acid and heated, the dry mass being dissolved in absolute alcohol. The alcoholic extract is then evaporated, the dry mass again dissolved in alcohol, and the extract allowed to evaporate on a shallow glass dish. The solid pellicle which remains is scraped off with a fine knife, and brought into the flame upon the thin platinum wire. For one experiment, $\frac{1}{10}$ of a milligramme is in general quite a sufficient quantity. Other compounds besides the silicates, in which small traces of lithium require to be detected, are transformed into sulphates by evaporation with sulphuric acid or otherwise, and then treated in the manner described.

In this way we arrive at the unexpected conclusion, that lithium is most widely distributed throughout nature, occurring in almost all bodies. Lithium was easily detected in 40 cubic centimetres of the water of the Atlantic Ocean, collected in 41° 41′ N. latitude, and 39° 14′ W. longitude. Ashes of marine plants (kelp), driven by the Gulf-stream on the Scotch coasts, contain evident traces of this metal. All the orthoclase and quartz from the granite of the Odenwald which we have examined contain lithium. A very pure spring water from the granite in Schlierbach, on the west side of the valley of the Neckar, was found to contain lithium, whereas the water from the red sandstone which supplies the Heidelberg laboratory was shown to contain none of this metal. Mineral waters, in a litre of which lithium could hardly be detected by the ordinary methods of analysis, gave plainly the line Li *a*, even if only a drop of the water on a platinum wire was

brought into the flame.* All the ashes of plants growing in the Odenwald on a granite soil, as well as Russian and other potashes, contain lithium. It was found also in the ashes of tabacco, of vine leaves, of the wood of the vine, and of grapes,† as well as in the ashes of the crops grown in the Rhine-plain near Waghäusel, Deidesheim, and Heidelberg, on a non-granitic soil. The milk of the animals fed upon these crops also contains lithium.‡

It is scarcely necessary to say that a mixture of volatile sodium and lithium salts gives the reaction of lithium alongside that of sodium with a scarcely perceptible diminution of precision and distinctness. The red lines of the former substance are still plainly seen when the bead contains $\frac{1}{1000}$ part of lithium salt, and when to the naked eye the yellow soda-flame appears untinged by the slightest trace of red. In consequence of the somewhat greater volatility of the lithium salt, the sodium reaction lasts longer than that of the other metal. In those cases, therefore, in which small quantities of lithium have to be detected in presence of large quantities of sodium, the bead must be brought into the flame whilst the observer is looking through the telescope. The lithium lines are often seen only for a few moments amongst the first products of the volatilization.

In the production of lithium salts on the large scale, in the proper choice of a raw material, and in the arrangement of suitable methods of separation, this spectrum-analysis affords most valuable aid. Thus it is only necessary to place a drop of mother-liquor from any mineral spring in the flame and to observe the spectrum produced, in order to show that in many of these waste products a rich and hitherto unheeded source of lithium salts exists. In the same way, during the course of the preparation, any loss of lithium in the collateral products and residues can be easily traced, and thus more convenient and economical methods of preparation may be found to replace those at present employed.§

Potassium.

Volatile potassium compounds give, when placed in the flame, a widely extended continuous spectrum, which contains only two characteristic lines, namely one line, Ka *a*, in the outermost red

* When liquids have to be brought into the flame, it is best to bend the end of the platinum wire, of the thickness of a horsehair, to a small ring, and to beat this ring flat. If a drop of liquid be brought into this ring, enough adheres to the wire for the experiment.

† In the manufactories of tartaric acid, the mother-liquors contain so much lithium salts that considerable quantities can thus be prepared.

‡ Dr. Folwarczny has been able, by help of the line Li *α*, to detect lithium in the ash of human blood and of muscular tissue.

§ We obtain by such an improved method from two jars (about 4 litres) of a mother-liquor from a mineral spring, which by evaporation with sulphuric acid gave 1k·2 of residue, half an ounce of carbonate of lithium of the purity of the commercial, the cost of which is about 140 florins the pound. A great number of other mineral-spring mother-liquors which we examined showed a similar richness in compounds of lithium.

approaching the ultra-red rays, exactly coinciding with the dark line A of the solar spectrum, and a second line, Ka β, situated far in the violet rays towards the other end of the spectrum, and also identical with a particular dark line observed by Fraunhofer. A very indistinct line coinciding with Fraunhofer's line B, which, however, is seen only when the light is very intense, is not by any means so characteristic. The violet line is somewhat pale, but can be used almost as well as the red line for the detection of potassium. Owing to the position of these two lines, both situated near the limit at which our eyes cease to be sensitive to the rays, this reaction for potassium is not so delicate as the reaction for the two metals already mentioned. It became visible in the air of our room when one gramme of chlorate of potassium mixed with milk-sugar was burnt. In this way, therefore, the eye requires the presence of $\frac{1}{1000}$ of a milligramme of chlorate of potassium in order to detect the presence of potassium.

Caustic potash, and all compounds of potassium with volatile acids, give the reaction without exception. Potash silicates, and other non-volatile salts, on the other hand, do not produce the reaction by themselves, unless the metal is present in very considerable quantity; when, however, the amount of potassium is smaller, it is merely necessary to melt the substance with a bead of carbonate of sodium. The presence of the sodium does not in the least interfere with the reaction, and scarcely diminishes its delicacy. Orthoclase, sanidine, and adularia may in this way be easily distinguished from albite, oligoclase, Labradorite, and anorthite. In order to detect the smallest traces of potassium salt, the silicate requires only to be slightly ignited with a large excess of fluoride of ammonium on a platinum capsule, after which the residue is brought into the flame on a platinum wire. In this way, it is found that almost every silicate contains potassium. Salts of lithium diminish or influence the reaction as little as sodium salts. Thus we need only to hold the end of a burnt cigar in the flame before the slit, in order at once to see the yellow line of sodium and the two red lines of potassium and lithium, this latter metal being scarcely ever absent in tobacco ash.

Strontium.

The spectra produced by the alkaline earths are by no means so simple as those produced by the alkalies. That of strontium is especially characterized by the absence of green bands. Eight lines in the strontium-spectrum are remarkable, namely, six red, one orange, and one blue line. The orange line, Sr α, which appears close by the sodium line towards the red end of the spectrum, the two red lines, Sr β and Sr γ, and lastly, the blue line, Sr δ, are the most important strontium bands, both as regards their position and their intensity. To examine the intensity of

the reaction, we quickly heated an aqueous solution of chloride of strontium, of known concentration, in a platinum dish over a large flame till the water was evaporated and the basin became red-hot. The salt then began to decrepitate, and was thrown up into the air, in microscopic particles in the form of a white cloud. On weighing the residual salt, it was found that in this way 0·077 grm. of chloride of strontium had been mixed in the form of a fine dust with the air of the room, weighing 77000 grms. As soon as the air in the room was perfectly mixed, by rapidly moving an open umbrella, the characteristic lines of the strontium-spectrum were beautifully seen. According to this experiment, a quantity of strontium may be thus detected equal to the $\frac{6}{100,000}$ part of a milligramme in weight.

The chloride and the other haloid salts of strontium give the best reaction. The hydrate and carbonate of strontium give it much less vividly, the sulphate still less, whilst the compounds of strontium with the non-volatile acids give either a very slight reaction or none at all. Hence it is well first to bring the bead of substance alone into the flame, and then again after moistening with hydrochloric acid. If it be supposed that sulphuric acid is present in the bead, it must be held in the reducing part of the flame before it is moistened with hydrochloric acid, for the purpose of changing the sulphate into the sulphide, which is decomposed by hydrochloric acid. To detect strontium when combined with silicic, phosphoric, boracic, and other non-volatile acids, it is best to proceed as follows:—Instead of fusing with carbonate of sodium in a platinum crucible, a conical spiral of platinum wire is employed; this spiral is heated to whiteness in the flame, and dipped while hot into finely-powdered dried carbonate of sodium which should contain so much water that a sufficient quantity adheres to the wire when it is once dipped into the salt. The fusion takes place in this spiral much more quickly than in a platinum crucible, as the mass of platinum requiring heating is small, and the flame comes into direct contact with the salt. As soon as the finely-powdered mineral has been brought into the fused soda by means of a small platinum spatula, and the mass retained above the melting point for a few minutes, the cooled mass has only to be turned upside down, and knocked on the porcelain plate of the lamp in order to obtain the salt in a large coherent bead. The fused mass is covered with a piece of writing paper, and then broken by pressing it with the blade of a steel spatula until the whole is reduced to a fine powder. The powder is brought to one spot on the edge of the plate, and carefully covered with hot water, which is allowed to flow backwards and forwards over it, so that, after decanting and rewashing the powder several times, all the soluble salts are extracted without losing any of the residue. If a solution of chloride of sodium be employed instead of water, the operation may be conducted more

rapidly and with greater security. The insoluble salt contains the strontium as carbonate; and one or two tenths of a milligramme of the substance, brought on to the wire and moistened with hydrochloric acid, is sufficient to produce the most intense reaction. It is thus possible, without help of platinum crucible, mortar, evaporating basin, or funnel and filter, to fuse, powder, digest, and wash out the substance in the space of a few minutes.

The reactions of potassium and sodium are not influenced by the presence of strontium. Lithium also can be easily detected in presence of strontium when the proportion of the former metal is not very small. The lithium line Li α appears as an intensely red sharply defined band upon a less distinct red ground of the broad strontium band Sr β.

Calcium.

The spectrum produced by calcium is immediately distinguished from the four spectra already considered by the very characteristic bright green line Ca β. A second no less characteristic feature in the calcium spectrum is the intensely bright orange line Ca α, lying considerably nearer to the red end of the spectrum than either the sodium line Na α, or the orange band of strontium Sr α. By burning a mixture consisting of chloride of calcium, chlorate of potassium, and milk-sugar, a white cloud is obtained which gives the reaction with as great a degree of delicacy as strontium salts do under similar circumstances. In this way it was found that $\frac{6}{10,000,000}$ of a milligramme in weight of chloride of calcium can be detected with certainty. Only the volatile compounds of calcium give this reaction; the more volatile the salt, the more distinct and delicate does the reaction become. The chloride, bromide, and iodide of calcium are in this respect the best compounds. Sulphate of calcium does not produce the spectrum till it has become basic, but then very brightly and continuously. In the same way the reaction of the carbonate becomes more distinctly visible after the carbonic acid has been expelled.

Compounds of calcium with the non-volatile acids remain inactive in the flame; but if they are attacked by hydrochloric acid, the reaction may easily be obtained as follows: A few milligrammes of the finely powdered substance are placed on the moistened flat platinum ring in the moderately hot portion of the flame, so that the powder is fritted, but not melted on to the wire; if a drop of hydrochloric acid be now allowed to fall into the ring, so that the greater part of the acid remains hanging to the wire, and if the wire be then brought into the hottest part of the flame, the drop evaporates in the spheroidal state without ebullition. If the spectrum of the flame be observed during this operation, it will be noticed that at the moment when the last particles of liquid evaporate, a bright calcium spectrum appears. If the quantities of the metal present are very small, the characteristic lines are

seen for a moment only; if larger quantities are contained, the phenomenon lasts for a longer time.

It is only in silicates which are decomposed by hydrochloric acid that the calcium can be thus detected. In those minerals which are not attacked by that acid, the examination is best made as follows. A few milligrammes of the substance under examination, in a state of fine division, are placed upon a flat platinum lid, together with about a gramme of fluoride of ammonium, and the mixture is gently ignited until all the fluoride is volatilized. The slight crust of salt remaining is moistened with a few drops of sulphuric acid, and the excess of acid removed by heat. If about a milligramme of the residual sulphates be scraped together with a knife, and brought into the flame, the characteristic spectra of potassium, sodium, and lithium, supposing these three metals to be present, are first obtained either simultaneously or consecutively. If calcium and strontium be also present, the corresponding spectra generally appear somewhat later, after the potassium, sodium, and lithium have been volatilized. When only traces of strontium and calcium are present, the reaction is not always seen; it becomes, however, immediately apparent on holding the bead for a few moments in the reducing flame, then moistening it with hydrochloric acid, and again bringing it into the flame.

These easy experiments, such as either heating the specimen alone, or after moistening with hydrochloric acid, or after treating the powder with fluoride of ammonium, either alone or in presence of sulphuric or hydrochloric acid, provide the mineralogist and geologist with a series of most simple methods of recognizing the components of the smallest fragment of many substances (such, for instance, as the double silicates containing lime) with a certainty which is attained in an ordinary analysis only by a large expenditure of time and material. The following examples will illustrate this statement.

1. A drop of sea-water heated on the platinum wire shows at first a strong sodium reaction; and after volatilization of the chloride of sodium, a weak calcium spectrum is observed, which on moistening the wire with hydrochloric acid becomes at once very distinct. If a few decigrammes of the residual salts obtained by the evaporation of sea-water be treated in the manner described under lithium with sulphuric acid and alcohol, the potassium and lithium reactions are obtained. The presence of strontium in sea-water can be best detected in the boiler-crust from sea-going steamers. The filtered hydrochloric acid solution of such a crust leaves, on evaporation and subsequent treatment with a small quantity of alcohol, a residue slightly yellow-coloured from basic iron salt, which is deposited after some days, and can then be collected on a small filter and washed with alcohol. The filter, burnt on a fine platinum wire and held in the flame, gives, besides the calcium lines, an intensely bright strontium spectrum.

2. Mineral waters often exhibit the reactions of potassium, sodium, lithium, calcium, and strontium by mere heating. If, for example, a drop of the Dürkheim or Kreuznach water be brought into the flame, the lines Na α, Li α, Ca α, and Ca β are at once seen. If, instead of using the water itself, a drop of the mother-liquor be taken, these bands appear most vividly. As soon as the chlorides of sodium and lithium have been to a certain extent volatilized, and the chloride of calcium has become more basic, the characteristic lines of the strontium spectrum begin to show themselves, and continue to increase in distinctness, until at last they come out in all their true brightness. In this case, therefore, by the mere observation of a single drop undergoing vaporization, the complete analysis of a mixture containing five constituents is performed in a few seconds.

3. The ash of a cigar moistened with hydrochloric acid, and held in the flame, shows at once the bands Na α, Ka α, Li α, Ca α, Ca β.

4. A piece of hard potash-glass combustion tubing gave, both with and without hydrochloric acid, the lines Na α and Ka α; treated with fluoride of ammonium and sulphuric acid, the bands Ca α, Ca β, and traces of Li α were rendered visible.

5. Orthoclase from Baveno gives, either alone or when treated with hydrochloric acid, only the line Na α with traces of Li α and Ka α; with fluoride of ammonium and sulphuric acid, the bright lines Na α and Ka α, and a somewhat less distinct Li α, are seen. After volatilization of the bodies thus detected, the bead moistened with hydrochloric acid gives a scarcely distinguishable flash of the lines Ca α and Ca β. The residue on the platinum wire, when moistened with cobalt solution and heated, gives the blue colour so characteristic of alumina. If the well-known reaction of silicic acid be likewise observed, we may conclude from this examination, made in the course of a very few minutes, that the orthoclase from Baveno contains silicic acid, alumina, potash with traces of soda, lime, and lithia; and also that no trace of baryta or strontia is present.

6. Adularia from St. Gothard comported itself in a similar manner, excepting that the calcium reaction was indistinctly seen, whilst that of lithium was altogether wanting.

7. Labradorite from St. Paul gives the sodium line Na α, but no calcium spectrum. On moistening the fragment with hydrochloric acid, the lines Ca α and Ca β appear very distinct; with the fluoride of ammonium test, a weak potassium reaction is obtained, and also faint indications of lithium.

8. Labradorite from the Corsican diorite gave similar reactions, except that no lithium was found.

9. Mosanderite from Brevig, and Tscheffkinite from the Ilmengebirge, showed, when treated alone, the sodium reaction; on the addition of hydrochloric acid, the lines Ca α and Ca β.

10. Melinophane from Lamoe gave the line Na *a* when placed alone in the flame; with hydrochloric acid, the lines Ca *a*, Ca *β*, and Li *a* became visible.

11. Scheelite and sphene, give on treatment with hydrochloric acid, a very intense calcium reaction.

12. When small quantities of strontium are present together with calcium, the line Sr *δ* may be most conveniently employed for the detection of this metal. In this way the presence of small quantities of strontium may be easily detected in very many sedimentary limestones. The lines Na *a*, Li *a*, Ka *a*, especially Li *a*, are observed as soon as the limestone is brought into the flame. Converted by hydrochloric acid into chlorides, and brought in this form into the flame, these minerals give the same bands; and not unfrequently the line Sr *δ* is also distinctly seen. This latter appears, however, only for a short time, and is in general best seen when the calcium spectrum begins to fade.

In this way, the lines Na *a*, Li *a*, Ka *a*, Ca *a*, Ca *β*, and Sr *δ* were found in the spectra of the following limestones:—

Limestone from the Silurian at Kugelbad near Prague. Muschelkalk from Rohrbach near Heidelberg. Limestone from the Lias at Malsch in Baden. Chalk from England.

The following limestones gave the lines Na *a*, Li *a*, Ka *a*, Ca *a*, Ca *β*, but not the blue strontium band Sr *δ*:—

Marble from the granite near Auerbach.* Devonian limestone from Gerolstein in the Eifel. Carboniferous limestone from Planitz in Saxony. Dolomite from Nordhausen in the Harz. Jura-kalk from Streitberg in Franconia.

From these few experiments, it is evident that a more extended series of exact spectrum analyses, respecting the amount of strontium, lithium, sodium, and potassium which the various limestone formations contain, must prove of the greatest geological importance, both as regards the order of their formation and their local distribution, and may possibly lead to the establishment of some unexpected conclusions respecting the nature of the oceans from which these limestones were originally deposited.

Barium.

The barium spectrum is the most complicated of the spectra of the alkalies and alkaline earths. It is at once distinguished from all the others by the green lines Ba *a* and Ba *β* (which are by far the most distinct) appearing the first and continuing during the whole of the reaction. Ba *γ* is not quite so distinct, but is still a well-marked and peculiar line. As the barium spectrum is considerably more extended than those of the other metals, the reaction is not observed to so great a degree of delicacy; still

* According to the method already described, a quantity of nitrate of strontium was obtained from 20 grms. of this marble such as to give a complete and vivid strontium spectrum. We have not examined the other limestones in the same way.

0·3 grm. of chlorate of barium burnt with milk-sugar gave a distinct band of Ba α which lasted for some time, when the air of the room was well mixed by moving an open umbrella about. Hence we may calculate, in the same manner as was done in the sodium experiment, that about $\frac{1}{1000}$ of a milligramme of barium salt may be detected with certainty.

The chloride, bromide, iodide, and fluoride, of barium, as also the hydrate, the sulphate, and carbonate, show the reaction best. It may be obtained by simply heating any of these salts in the flame.

Silicates containing barium, which are decomposed by hydrochloric acid, also give the reaction if a drop of hydrochloric acid be added to them before they are brought into the flame. Baryta-harmotome, treated in this way, gives the lines Ca α and Ca β, together with the bands Ba α and Ba β.

Compounds of barium with fixed acids, giving no reaction either when alone or after addition of hydrochloric acid, should be fused with carbonate of sodium, as described under strontium, and the carbonate of barium thus obtained, examined. If barium and strontium occur in small quantities together with large amounts of calcium, the carbonates obtained by fusion are dissolved in nitric acid, and the dried salt extracted with alcohol. The residue contains only barium and strontium, both of which can almost always be detected. When we wish to test for small traces of strontium or barium, the residual nitrates are converted into chlorides by ignition with sal-ammoniac, and the chloride of strontium is extracted by alcohol. Unless the quantity of one or more of the bodies to be detected is extremely small, the methods of separation just described are quite unnecessary, as is seen from the following experiment:—

A mixture of the chlorides of potassium, sodium, lithium, calcium, strontium, and barium, containing at the most $\frac{1}{10}$ of a milligramme of each of these salts, was brought into the flame, and the spectra produced were observed. At first the bright yellow sodium line Na α appeared, with a background formed by a nearly continuous pale spectrum. As soon as this line began to fade, the exactly defined bright red line of Lithium Li α was seen; and beyond this, still farther from the sodium line, the faint red potassium line Ka α was noticed, whilst the two barium lines, Ba α, Ba β, with their peculiar shading, became distinctly visible in their characteristic places. As the potassium, sodium, lithium, and barium salts volatilized, their spectra became fainter and fainter, and their peculiar bands one after the other vanished, until, after the lapse of a few minutes, the lines Ca α, Ca β, Sr α, Sr β, Sr γ, and Sr δ, became gradually visible, and like a dissolving view, at last attained their characteristic distinctness, colouring, and position, and then after some time, became pale and disappeared entirely.

The absence of any one or of several of these bodies is at once indicated by the non-appearance of the corresponding bright lines.

Those who become acquainted with the various spectra by repeated observation, do not need to have before them an exact measurement of the individual lines in order to be able to detect the presence of the various constituents; the colour, relative position, peculiar form, variety of shade and brightness of the bands are quite characteristic enough to ensure exact results, even in the hands of persons unaccustomed to such work. These special distinctions may be compared with the differences of outward appearance presented by the various precipitates employed for detecting substances in the wet way. Just as a precipitate is characterized as gelatinous, pulverulent, flocculent, granular, or crystalline, so the lines of the spectrum exhibit their peculiar aspects, some appearing sharply defined at their edges, others blended off either at one or both sides, either similarly or dissimilarly, some, again, appearing broader, others narrower; and just as in ordinary analysis we make use of those precipitates only which are produced with the smallest possible quantity of the substance supposed to be present, so in analysis with the spectrum, we employ only those lines which are produced by the smallest possible quantity of substance and require a moderately high temperature. In these respects, both analytical methods stand on an equal footing; but analysis with the spectrum possesses a great advantage over all other methods, inasmuch as the characteristic differences of colour of the lines serve as the distinguishing feature of the system. Most of the precipitates which are valuable as reactions are colourless; and the tint of those which are coloured varies very considerably according to the state of division and mechanical arrangement of the particles. The presence of even the smallest quantity of impurity is often sufficient entirely to destroy the characteristic colour of a precipitate; so that no reliance can be placed upon nice distinctions of colour as an ordinary chemical test. In spectrum-analysis, on the contrary, the coloured bands are unaffected by such alteration of physical conditions, or by the presence of other bodies. The positions which the lines occupy in the spectrum indicate the existence of a chemical property as unalterable as the combining weights themselves, and may therefore be estimated with almost astronomical precision. The fact, however, which gives to this method of spectrum-analysis a peculiar degree of importance is, that it extends almost to infinity, the limits within which the chemical characteristics of matter have been hitherto confined. By an application of this method to geological inquiries concerning the distribution and arrangement of the components of the various formations, the most valuable results may be expected; even the few random experiments already mentioned have led to the unexpected conclusion, that not only potassium and sodium, but also lithium and strontium must be added to the list of bodies occurring, only indeed in small quantities, but most widely spread, throughout the matter composing the solid body of our planet.

The method of spectrum-analysis may also play a no less important part as a means of detecting new elementary substances; for if bodies should exist in nature so sparingly diffused that the analytical methods

hitherto applicable have not succeeded in detecting or separating them, it is very possible that their presence may be revealed by a simple examination of the spectra produced by their flames. We have had opportunity of satisfying ourselves that in reality such unknown elements exist. We believe that, relying upon unmistakeable results of the spectrum-analysis, we are already justified in positively stating that, besides potassium, sodium, and lithium, the group of the alkaline metals contains a fourth member, which gives a spectrum as simple and characteristic as that of lithium—a metal which in our apparatus gives only two lines, namely a faint blue one, almost coincident with the strontium line Sr δ, and a second blue one lying a little further towards the violet end of the spectrum, and rivalling the lithium line in brightness and distinctness of outline.

The method of spectrum-analysis not only offers, as we think we have shown, a mode of detecting with the greatest simplicity the presence of the smallest traces of certain elements in terrestrial matter, but it also opens out the investigation of an entirely untrodden field, stretching far beyond the limits of the earth, or even of our solar system. For, in order to examine the composition of luminous gas, we require, according to this method, only to see it; and it is evident that the same mode of analysis must be applicable to the atmospheres of the sun and of the brighter fixed stars. A modification must, however, be introduced on account of the light emitted by the solid nuclei of these heavenly bodies. In a Memoir published by one of us,* "On the relation between the Coefficients of Emission and Absorption of Bodies for Heat and Light," it was proved from theoretical considerations that the spectrum of an incandescent gas becomes *reversed* (that is, that the bright lines become changed into dark ones) when a source of light of sufficient intensity, giving a continuous spectrum, is placed behind the luminous gas. From this we may conclude that the solar spectrum, with its dark lines, is nothing else than the reverse of the spectrum which the sun's atmosphere alone would produce. Hence, in order to effect the chemical analysis of the solar atmosphere, all that we require is to discover those substances which, when brought into the flame, produce bright lines coinciding with the dark ones of the solar spectrum.

In the paper above referred to, the following experimental facts are given in confirmation of the preceding theoretical conclusion.

The bright red line produced in the spectrum of a gas-flame by the presence of a bead of chloride of lithium, is changed into a dark one when direct sunlight is allowed to pass through the flame. When the bead of lithium is replaced by one of chloride of sodium, the dark double line D (coincident with the yellow sodium line) appears with uncommon distinctness. The dark double line D also appears when the rays of a Drummond's light are passed through the flame of aqueous alcohol into which chloride of sodium is thrown.†

* Kirchhoff, Poggendorff's Annalen, cix. 275; and Phil. Mag. [4], xx. 1.

† In the Philosophical Magazine for March 1860, Prof. Stokes calls attention to the fact that in the year 1849, Foucault made an observation very similar to the above. In the examination of the spectrum produced by the electric arc between carbon points, Foucault noticed that bright lines occur where the double line D of the solar spectrum is found, and that this dark line D is produced or made more intense when the rays of the sun, or those from one of the incandescent carbon poles, are passed through the luminous arc. The observation mentioned in the text affords

It appeared of interest to obtain still further confirmation of this important theoretical conclusion; the following experiments answered this purpose:

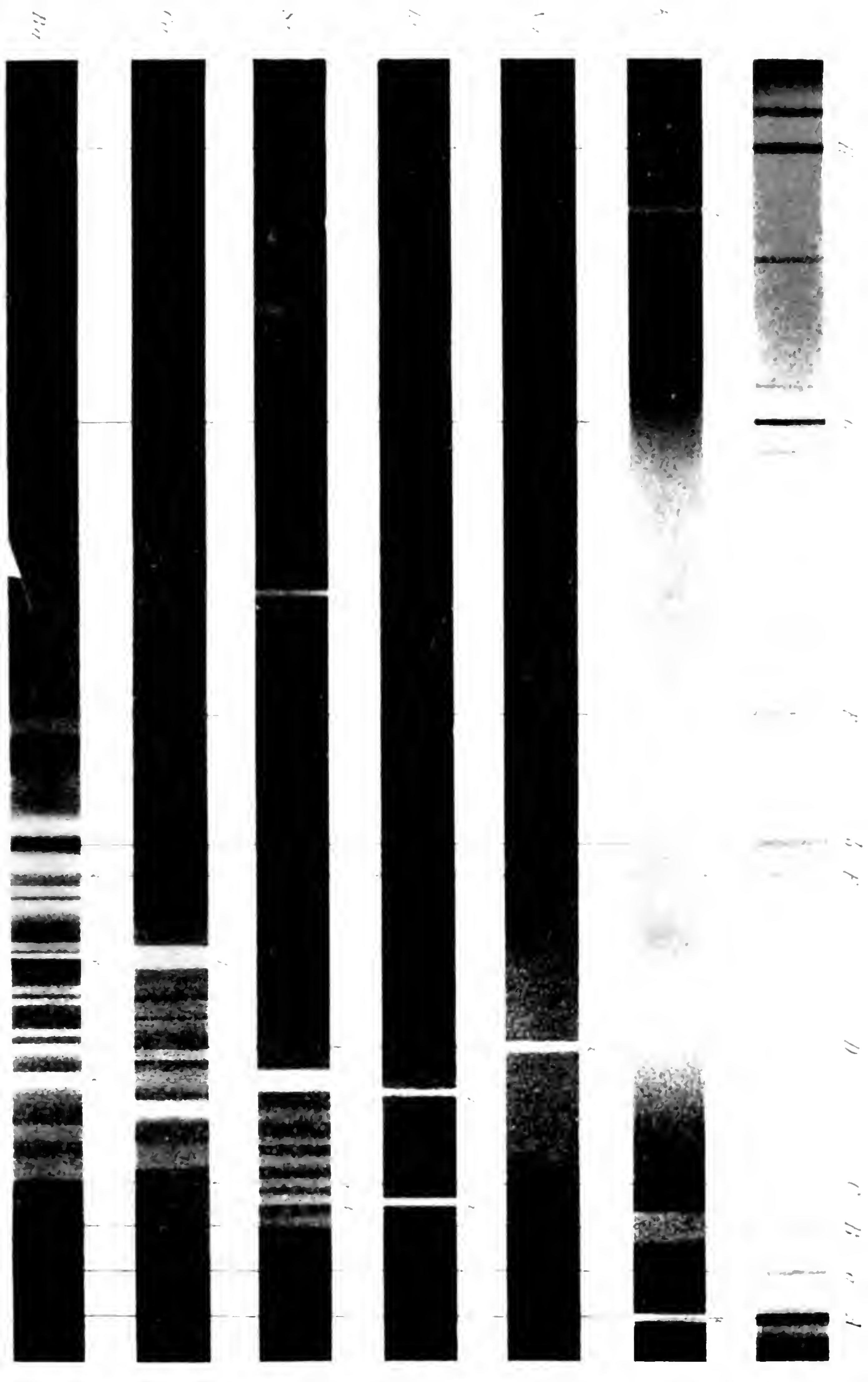
We ignited a thick platinum wire in the flame, and then by means of an electric current, heated it to a temperature approaching its melting-point. The wire gave a bright spectrum, in which no trace of either dark or bright lines was seen. A flame of weak aqueous alcohol, in which common salt was dissolved, on being brought between the wire and the slit of the apparatus, gave the dark line D most distinctly.

The dark line D can be produced in the spectrum of a platinum wire heated in a flame, by holding between flame and spectrum a test-tube containing some sodium amalgam which is heated to boiling.

This experiment is important, because it shows that sodium vapour at a temperature much below that at which it becomes luminous, exerts its absorptive power at exactly the same point of the spectrum as it does at the highest temperatures which we can produce, or at the temperatures existing in the solar atmosphere.

We have succeeded in reversing the bright lines in the spectra of K, Sr, Ca, Ba, by employing sunlight and mixtures of the chlorates of these metals with milk-sugar. A small iron trough was fixed in front of the slit of our apparatus, in which the mixture was placed; the direct sunlight was then allowed to pass along the whole length of the trough, and the mixture was ignited with a heated wire. The telescope C, with the wires cutting each other at an oblique angle, was placed so that the point of intersection of the wires coincided with the bright line of the flame-spectrum which was to be examined. The observer concentrated his attention upon this point, to judge whether, at the moment of burning the mixture, a dark line showed itself passing through the point of intersection of the cross wires. In this way it was easy, when the right proportions for the mixtures were found, to show that the lines Ba α, Ba β, as well as the line Ka β, were reversed. The last of these lines coincides with one of the most distinct dark lines in the solar spectrum, though not marked by Fraunhofer, which, however, appears much more plainly than it is generally seen at the moment the potash salt burns. In order to prove that the strontium lines can be reversed, the chlorate of strontium must be most carefully dried, as the slightest trace of moisture produces a positive strontium spectrum, owing to small particles of salt being thrown about in the flame, and thus diminishing the power of the solar rays.

an explanation of this interesting phænomenon observed by Foucault eleven years ago, proving that it is not occasioned by the properties of the electric light, which in many respects is still so enigmatical, but that it arises from a compound of sodium contained in the pole, and converted into incandescent gas by the current.



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XXV.—*Contributions to the History of the Phosphorus-Bases.*

BY AUGUSTUS WILLIAM HOFMANN, F.R.S.

[Abstracted from a series of papers read before the Royal Society, June 21, 1860.]

FIRST MEMOIR.

IN a paper* published a few years ago by M. Cahours and myself, the remarkable phosphorus-compounds, whose existence was first pointed out by the experiments of M. Paul Thénard, were subjected to a more complete examination than they had previously received.

The discovery of a better mode of preparation enabled us to gain a clearer view of the nature of this group of substances, and to throw additional light on their relations to the nitrogen-bases; but, owing to the overwhelming number of reactions which presented themselves, we were unable to submit the behaviour of the phosphorus-bases with other groups of bodies to a detailed examination.

In continuation of former experiments, I have lately been much engaged in the investigation of the polyatomic ammonias, the study of which was naturally suggested by the beautiful researches

* Philosophical Transactions, vol. cxlvii, p. 575. Chem. Soc. Qu. vol. xi, p. 56.

which have been published on the polyatomic alcohols. In the course of these experiments, I frequently had occasion to return to the phosphorus-bases, the employment of triethylphosphine in particular having in many instances led to results which would not easily have been obtained in any other way. The possibility of preparing this body in a state of perfect purity and in considerable quantity, by a series of processes, which, if not quite simple, are at least definite and certain, its position in the system of organic compounds, its conveniently situated boiling-point, the energy and precision of its reactions, and lastly, the simplicity which characterizes these reactions, in consequence of the absence of unreplaced hydrogen in triethylphosphine,—whereby the formation of a large number of compounds of subordinate theoretical interest is excluded,—all these conditions tend strongly to invite us to the study of a body, in whose chemical relations the leading questions of the day are not unfrequently mirrored with surprising distinctness.

It was originally my intention to put together—in one frame, as it were—the various facts which I have collected relating to the phosphorus-bases; but the material lies scattered in so many directions, that I deem it more advisable to publish these observations in a number of shorter memoirs, which, from the nature of the subject, must be more or less fragmentary.

Preparation of Triethylphosphine.—The whole of the material used in my experiments was prepared by the process formerly described in detail by Cahours and myself. The only alteration, which has been found advisable, relates to the separation of the triethylphosphine from the chloride-of-zinc-compound, which is produced by the action of trichloride of phosphorus on zinc-ethyl. It was formerly our practice to throw solid hydrate of potassium into the viscid mass of this salt, and then to dissolve the potassa by gradually dropping water into the retort, the heat resulting from the reaction being sufficient to carry over the base nearly anhydrous. It is better, however, to mix the double salt at once with water, and then decompose it in a retort filled with hydrogen, by allowing strong potassa-solution slowly to flow into it. On subsequently distilling the mixture on a sand bath in a continuous but very slow stream of hydrogen, the triethylphosphine passes over with the aqueous vapour and floats on the top of the con-

densed water in the receiver. By adopting this mode of proceeding, the reaction is more under the command of the operator, and as the phosphorus-base is not sensibly soluble in water, the quantity of the product is not thereby diminished.

By exact adherence to the prescribed conditions, it is by no means difficult to prepare considerable quantities of pure triethylphosphine; nevertheless the amount obtained is always less than it should be in proportion to the weight of the materials used. This loss is mainly due to the formation of secondary products, which cannot be wholly avoided even when the zinc-ethyl has been carefully prepared, and to partial decomposition of the latter substance during distillation: for it is scarcely possible to imagine a more elegant reaction than that which takes place between trichloride of phosphorus and ready-formed zinc-ethyl. Under these circumstances, many attempts were naturally made to obtain the phosphorus-base in other ways; I have always, however, returned to our original process.

Totally unsuccessful was the attempt to obtain triethylphosphine, without previous preparation of zinc-ethyl, by exposing a mixture of 1 equiv. of trichloride of phosphorus and 3 equivs. of iodide of ethyl with excess of zinc in sealed tubes to a temperature of 150° C. The bodies react under these circumstances; but as only traces of triethylphosphine are produced, I have not thought it worth while to pursue this reaction further. A more favourable result was obtained by heating a mixture of zinc and phosphorus with anhydrous iodide of ethyl to between 150° and 160°. After several hours' digestion, the tubes were found to be coated with white crystals, and a considerable portion of the phosphorus had passed into the red modification. Powerful escape of gas always took place on opening the tubes, and in several instances they were shattered, even when their points were softened in the lamp-flame to diminish the violence of the concussion. Besides zinc-ethyl, the presence of which is indicated by the abundant evolution of hydride of ethyl which is observed on treating the contents of the tube with water, the chief products of this reaction are three phosphorus-compounds, which are formed in proportions varying according to the temperature and the duration of the action.

On extracting the brown residue in the tubes with warm water, and evaporating the clear solution, an oily substance separates

which covers the bottom of the dish, and on cooling solidifies into a mass of hard crystals. By repeatedly crystallizing this substance from boiling water and from alcohol, large crystals are obtained, which give off triethylphosphine when treated with potassa even in the cold; by analysis* they were found to consist of a compound of iodide of zinc with iodide of triethylphosphonium, composed according to the formula

$$C_6H_{16}P\,Zn\,I_2 = [(C_2H_5)_3H\,P]I, Zn\,I.†$$

A solution of iodide of triethylphosphonium mixed with iodide of zinc immediately gives a crystalline compound of exactly similar characters.

The mother-liquor of the double salt yields, when further evaporated, another crystalline body which is more difficult to purify. After three or four crystallizations, however, well-developed crystals are obtained, which do not yield triethylphosphine when treated with potash, either in the cold or with aid of heat.

Analysis shows that this crystalline substance is a compound of iodide of zinc and oxide of triethylphosphine,

$$C_6H_{15}PO, ZnI = (C_2H_5)_3PO, ZnI.$$

The third compound, which remains in the mother-liquor after the two former have crystallized out, and separates, on further evaporation, in beautiful needle-shaped crystals, may be recognized without difficulty as iodide of tetrethylphosphonium. The crystals are insoluble in cold potassa-solution, and give off triethylphosphine only when heated with solid hydrate of potassium.

This iodide likewise unites with iodide of zinc; and as this latter salt is always present in the mother-liquor in considerable quantity, the double salt is generally obtained together with the simple iodide.

* The combustion of the phosphorus-compounds is not very easily effected. The experiment succeeds best with a mixture of chromate of lead and oxide of copper. All the carbon-determinations quoted in the following pages have been made with this mixture, unless another mode of proceeding is specially stated. All the substances analysed were dried at 100°, except in a few cases, when the mode of drying is also specially mentioned.

The details of the analytical determinations are given in the original papers published in the Philosophical Transactions for 1860.

† H=1; O=16; S=32; C=12.

The mode of formation of these compounds is represented by the following equations:—

$$4C_2H_5I + P + 3Zn = [(C_2H_5)_3HP]I, Zn\,I + 2Zn\,I + C_2H_4.$$
$$4C_2H_5I + P + 3Zn = [(C_2H_5)_4P]I, ZnI + 2ZnI.$$

The compound containing oxide of triethylphosphine is evidently formed at the expense of the air in the tube:—

$$(C_2H_5)_3P + O + Zn\,I = (C_2H_5)_3PO, Zn\,I.$$

The above zinc-iodide-compounds of triethyl- and tetrethyl-phosphonium possess interest only in so far as they may serve for the preparation of phosphorus-base. The mixture evaporated to dryness and distilled with hydrate of potassium in an atmosphere of hydrogen, does indeed yield appreciable quantities of triethylphosphine: the action of iodide of ethyl upon a mixture of zinc and phosphorus may therefore be recommended when it is desired to prepare a sample of this remarkable compound without specially arranged apparatus: but it is not adapted for the preparation of the phosphorus-base on the large scale.

I have endeavoured to prepare by this process *triamylphosphine* and *triallylphosphine*, but the results were not such as to encourage me to continue the experiments.

Cahours has recently made similar experiments, but with a difference in the mode of conducting them, which cannot fail to influence the result. Instead of subjecting iodide of ethyl to the action of a mechanical mixture of zinc and phosphorus, he has caused the compound Zn_3 P to act upon iodide of ethyl at a high temperature. The reaction will doubtless proceed more regularly under these conditions; but the advantage which may perhaps be gained by avoiding the preparation of the zinc-ethyl is compromised, at least in part, by the time and trouble expended in the somewhat complicated preparation of trizinco-phosphide.

Oxide of Triethylphosphine.—The formation of the compound of this oxide with iodide of zinc to which I have alluded, induced me to subject to a careful examination the beautifully crystallized body produced from the phosphorus-base by exposure to the air.

In our former experiments, Cahours and myself had often observed this substance, but we did not succeed in obtaining it in

a state of purity fit for analysis. Nevertheless, founding our conclusion on the composition of the corresponding sulphur-compound, and having regard to the analogies presented by the bodies of the arsenic- and antimony-series, we regarded this body as the oxide of the phosphorus-base:

$$C_6H_{15}PO = (C_2H_5)_3PO.$$

I have since confirmed this formula by analysis.

The difficulties which in our former experiments opposed the preparation of this compound in the pure state, arose entirely from the comparatively small quantity of material with which we had to work. Nothing is easier than to obtain this oxide in a state of purity, provided the available quantity of material is sufficient for distillation. In the course of a number of preparations of triethylphosphine for the new experiments, a considerable quantity of the oxide had accumulated in the residues left after distilling the zinc-chloride-compound with potassa. On subjecting these residues to distillation in a copper retort, a considerable quantity of the oxide passed over with the aqueous vapours; and a further quantity was obtained as a tolerably anhydrous but strongly coloured liquid by dry distillation of the solid cake of salts which remained after all the water had passed over. The watery distillate, with or without addition of hydrochloric acid, was evaporated on the water-bath as far as practicable, and the concentrated solution was mixed with solid hydrate of potassium, which immediately separated the oxide in the form of an oily layer floating on the surface of the potash.

The united products were then left in contact with solid potash for twenty-four hours, and again distilled. The first portion of the distillate still contained traces of water, a thin layer of triethylphosphine floating upon the surface. As soon as the distillate solidified, the receiver was changed, and the remaining portion (about nine-tenths) collected apart as the pure product.

With reference to the properties of oxide of triethylphosphine, I may add the following statements to the description formerly given*. This substance crystallizes in beautiful delicate needles, which, if an appreciable quantity of the fused compound be allowed to cool slowly, frequently attain the length of several inches. I have been unable to obtain well-formed crystals; as yet I have not

* Philosophical Transactions, 1857. p. 586; Chem. Soc. Qu., vol. xi, p. 66.

found a solvent from which this substance can be crystallized. It is soluble in all proportions, both in water and alcohol, and separates from these solvents on evaporation in the liquid condition, and solidifies only after every trace of water or alcohol is expelled.

Addition of ether to the alcoholic solution precipitates this body likewise as a liquid. The melting point of oxide of triethylphosphine is 44°; the point of solidification at the same temperature. It boils at 240° C. (corrected).

As no determination of the vapour-density of any member of the group of compounds to which the oxide of triethylphosphine belongs has yet been made, it appeared to me of some interest to perform this experiment with the oxide in question. As the quantity of material at my disposal was scarcely sufficient for the determination by Dumas' method, and Gay-Lussac's was inapplicable on account of the high boiling-point of the compound, I adopted a modification of the latter, consisting essentially in generating the vapour in the closed arm of a U-shaped tube filled with mercury and immersed in a copper vessel containing heated paraffin, and calculating its volume from the weight of the mercury driven out of the other arm. As I intend to publish a full description of this method, which promises to be very useful in certain cases, I shall here content myself with stating that the results of my experiments prove the vapour-density of oxide of triethylphosphine to be 66·30, referred to hydrogen as unity, or 4·60 referred to atmospheric air. Assuming that the molecule of oxide of triethylphosphine corresponds to 2 vols. of vapour,* the calculated specific gravity of its vapour $= \frac{134}{2} = 67$, when referred to hydrogen, and 4·63 when referred to air. Hence we may conclude that in oxide of triethylphosphine, the elements are condensed in the same manner as in the majority of thoroughly investigated organic compounds.

From the facility with which triethylphosphine is converted into the oxide by exposure to the air, even at ordinary temperatures, and from the very high boiling-point of the resulting compound, in consequence of which its vapour can exert but very slight tension at ordinary temperatures, I am induced to think that the phosphorus-base may be used in many cases for the volumetric estimation of oxygen. When a paper ball soaked in triethylphos-

* $H_2O = 2$ vols. of vapour.

phine is passed up into a portion of air confined over mercury, the mercury immediately begins to rise, and continues to do so for about two hours, after which the volume becomes constant, the diminution corresponding very nearly to the proportion of oxygen in the air. To obtain very exact results, however, it would probably be necessary in every case to remove the residual vapour of triethylphosphine by means of a ball saturated with sulphuric acid.

Oxide of triethylphosphine exhibits in general but small tendency to unite with other bodies; nevertheless it forms crystalline compounds with iodide and bromide of zinc. I have examined more particulaly the zinc-iodide-compound already mentioned.

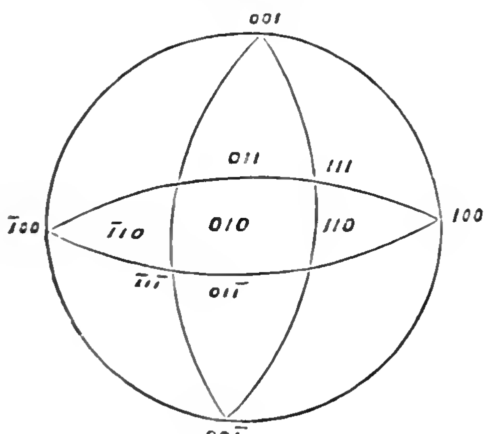
Oxide of Triethylphosphine and Iodide of Zinc.—On mixing the solutions of the two bodies, the compound separates either as a crystalline precipitate or in oily drops, which soon solidify with crystalline structure. It is easily purified by recrystallization from alcohol and contains—

$$C_6H_{15}PO, ZnI = (C_2H_5)_3PO, ZnI.$$

It is remarkable that this compound is formed in presence of a large excess of hydriodic and even of hydrochloric acid.

The crystals melt at 99°: they readily dissolve in warm water, and even more easily in alcohol. From the alcoholic solution well-formed crystals are frequently obtained.

Fig. 1.



My friend Quintino Sella has examined these crystals.*

" System monoclinic:—
100, 101 = 34° 25′; 101, 001 = 48° 48′;
111, 010 = 50° 16′.

Forms observed:—
100, 010, 001, 110, 011, 111, (Fig. 1).

Combinations observed:—

110, 001 (Fig 2).
110, 001; 100 (Figs. 3 & 4).
110, 001; 100, 010 (Fig. 5).
001, 100, 110, 111.
001, 100, 110, 111; 011.
001, 100, 110, 111; 011, 010 (Fig. 6).

* The details of the crystallographical determinations are given in the original papers published in the Philosophical Transactions for 1860.

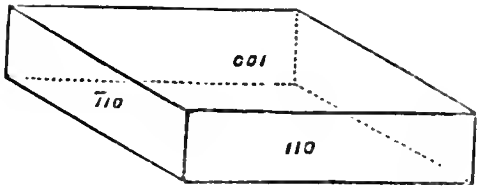


Fig. 2.

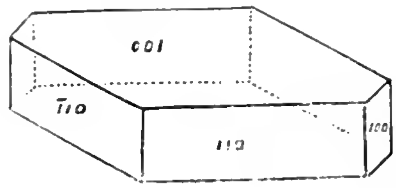


Fig. 3.

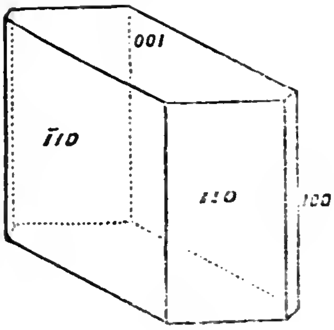


Fig. 4.

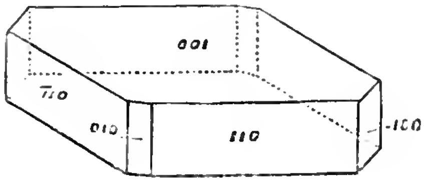


Fig. 5.

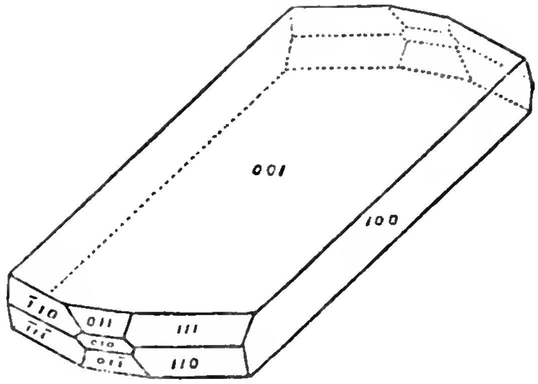


Fig. 6.

Hemitropic crystals with the axis of hemitropy [100], with the face of hemitropy 001.

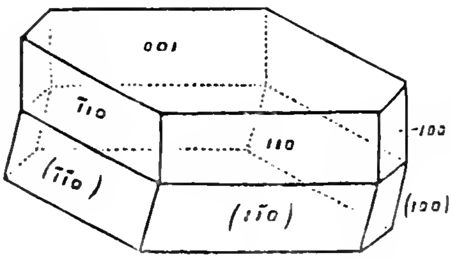


Fig. 7.

The hemitropic crystals are sometimes simple, as in Fig. 7; sometimes complicated, as in Fig. 8. It is then difficult to distinguish them from trimetric crystals; they become, however, intelligible by assuming that they result from four hemitropic crystals grouped round [100], as in Fig. 9. It is found sometimes that several crystals, like those of Fig. 8, are associated by 001.

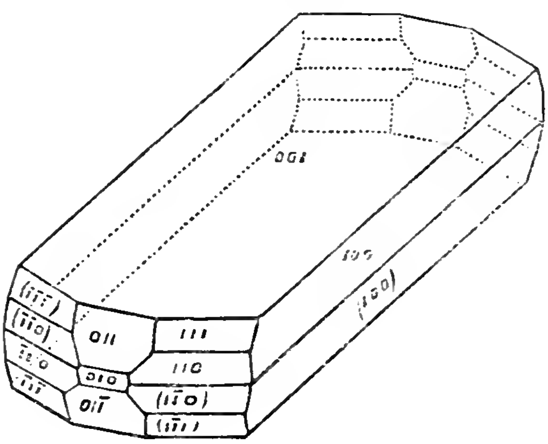


Fig. 8.

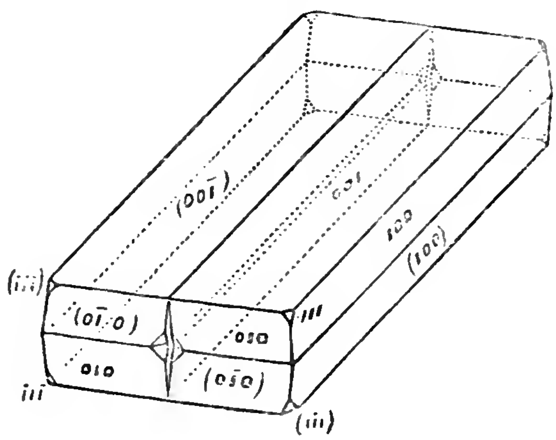


Fig. 9.

It deserves to be noticed that the crystals (Figs. 2, 3, 4, 5, and 7) were formed in the presence of hydrochloric acid, and that in

the absence of this acid, only crystals of Fig. 8 are obtained, which, without the study of the cleavage and the optical characters, could not be distinguished from trimetric crystals.

Cleavages 001 and 110 neat and easy. The cleavage 110 of the hemitropic crystals (Fig. 8) exhibits re-entering angles.

Lustre vitreous on the fracture, fatty on the faces.

Hardness somewhat greater than that of gypsum.

The crystals are optically positive; the line of symmetry [010] is their principal medium line. The internal angle of the optical axes differs but little from 78°: and the plane which contains them is nearly perpendicular to the edge of the prism 110.

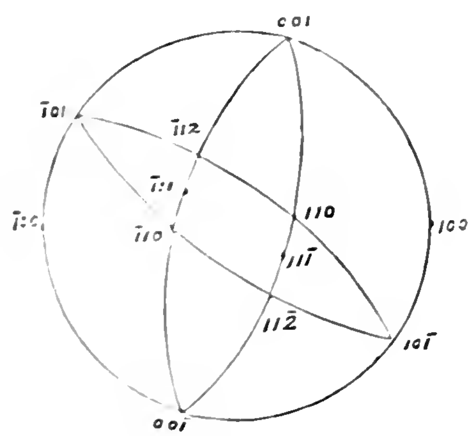
The smallest index of refraction is approximately $\gamma = 1{\cdot}58$."

Oxide of Triethylphosphine and Dichloride of Platinum.—No precipitate is formed on mixing the aqueous solutions of the two compounds, however concentrated; but on adding the anhydrous oxide to a concentrated solution of dichloride of platinum in absolute alcohol, a crystalline platinum-compound is deposited after a few moments. This compound is exceedingly soluble in water, easily soluble in alcohol, insoluble in ether. On adding ether to the alcoholic solution, the salt is precipitated, although with difficulty, in the crystalline state. The alcoholic solution, when evaporating spontaneously, yields beautiful hexagonal plates, frequently of rather large dimensions. On account of its extreme solubility, it is not quite easy to obtain this salt in considerable quantity.

Analysis has led to the somewhat complicated formula

$$C_{24}H_{60}P_4O_3Pt_2Cl_6 = 3[(C_2H_5)_3PO], (C_2H_5)_3PCl_2, 2PtCl_2.$$

Fig. 10.



The platinum-salt has likewise been examined by Quintino Sella.

"System monoclinic:—
100, 101 = 27° 19′; 101, 001 = 46° 23′; 010, 111 = 41° 4′.

Forms observed:—
100, 001, 110, 101, 111, 112 (Fig. 10.)

Combinations observed :—

001, 100, 110. (Fig. 11).

001, 110, $\bar{1}12$, $\bar{1}01$.

001, 110, $\bar{1}12$, $\bar{1}01$, 100, $\bar{1}11$ (Fig. 12).

Fig. 11.

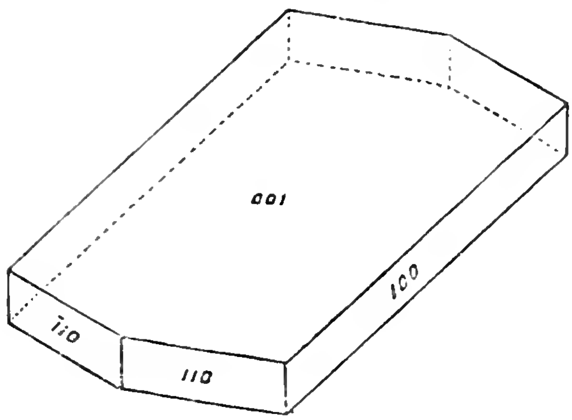
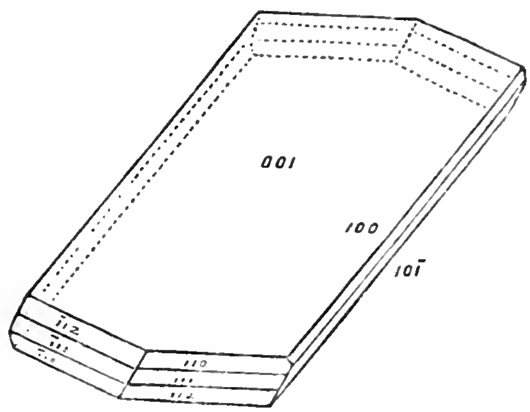


Fig. 12.



Cleavages $\bar{1}01$ and 110 neat and easy.

Colour orange-red.

The optical axes are situated in 010, *i. e.* in the plane of symmetry. They are seen across the faces 001 and the cleavages $\bar{1}01$, and they make an apparent angle of about 64°."

On mixing a concentrated solution of the oxide of triethylphosphine with *trichloride of gold,* a deep-yellow oil is separated, which crystallizes with difficulty after considerable standing. This compound is exceedingly soluble in water and in alcohol. When the aqueous solution is heated, the gold is reduced; the transformation which the oxide of triethylphosphine undergoes in this reaction has not been examined.

Chloride of Tin forms likewise an oily compound with the oxide: I have not succeeded in crystallizing this compound.

Chloride of Mercury is without any action on oxide of triethylphosphine.

Oxychloride of Triethylphosphine.—On passing a current of dry hydrochloric acid through a layer of oxide of triethylphosphine which is fused in a U-shaped tube surrounded by boiling water, brilliant crystals are soon formed. These crystals, however, rapidly disappear, the compound formed in the commencement of the reaction uniting with an excess of hydrochloric acid. The

viscous liquid which ultimately remains behind, loses, when heated, the excess of hydrochloric acid, leaving an exceedingly deliquescent crystalline mass, very soluble in alcohol, insoluble in ether.

For analysis, the new compound was washed with absolute ether, and dried over sulphuric acid *in vacuo*, either at the common temperature or at 40°. Three chlorine-determinations in specimens of different preparations led to the formula

$$C_{12}H_{30}P_2OCl_2 = (C_2H_5)_3PO + (C_2H_5)_3PCl_2,$$

which represents an oxychloride of triethyphosphine. The dichloride of triethylphosphine cannot be formed by the action of hydrochloric acid upon the oxide.

The oxychloride exhibits with other compounds the deportment of the oxide. It furnishes with dichloride of platinum the same platinum-salt which is obtained with the oxide. In a similar manner it gives with iodide of zinc the iodide-of-zinc-compound of the oxide previously described. Only once—under conditions not sharply enough observed at the time, and which I was afterwards unable to reproduce in repeated experiments—a compound of the oxychloride with iodide of zinc was formed. This substance, readily soluble in water and alcohol, crystallized from the latter solvent in beautiful colourless transparent octahedra, which, on analysis, gave results, leading to the formula,

$$C_{12}H_{30}P_2OCl_2Zn_2I_2 = (C_2H_5)_3PO,ZnI + (C_2H_5)_3PCl_2,ZnI.$$

Behaviour of Triethylphosphine with Sulphur-compounds.—The remarkable tendency of the phosphorus-base to unite with sulphur has already been mentioned in the previous memoir: the combination of the two bodies is attended with evolution of heat, the result being a beautifully crystalline substance,

$$C_6H_{15}PS = (C_2H_5)_3PS,$$

corresponding to the oxide of triethylphosphine.

This behaviour has induced me to study the action of several sulphur-compounds on the phosphorus-base. In the cases which I have examined, the ultimate product is almost invariably the sulphide of triethylphosphine, already mentioned as resulting from the direct combination of the phosphorus-base with sulphur; but

the conditions under which this sulphide is produced vary considerably; and in the majority of cases, it occurs only as a secondary product of the decomposition of other more direct compounds, some of which appeared to me sufficiently interesting to deserve more minute investigation.

In the course of the experiments which I am going to describe, I have prepared considerable quantities of the sulphide of triethylphosphine. This compound, although remarkable for the facility with which it crystallizes, is not easily procured in well-formed crystals. It was only once or twice that I obtained crystals with good faces. They were examined by Quintino Sella, who communicates to me the following results:—

" System rhombohedric:—

$$100,\ 111 = 54^\circ\ 35'.$$

Forms observed:—

$$10\bar{1},\ 2\bar{1}\bar{1},\ 210\ \text{(Fig. 13)}.$$

Combinations observed:—

$$10\bar{1},\ 210\ \text{(Fig. 14)}.$$
$$10\bar{1},\ 210;\ 2\bar{1}\bar{1}.$$

Fig. 13.

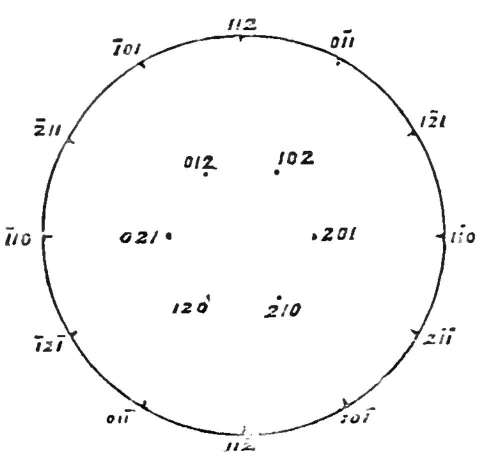
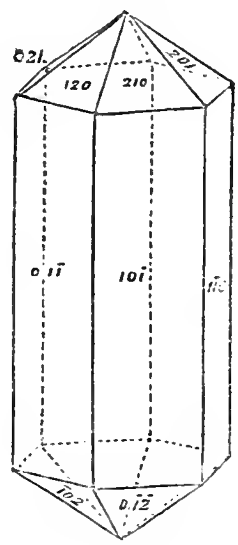


Fig. 14.



At summer heat, the crystals are very soft and flexible; they may be bent 180° without breaking. At lower temperatures, they are harder and much less flexible.

The crystals are optically positive. The index of refraction for the extraordinary ray $\epsilon = 1°65$, and for the ordinary ray $\omega = 1{\cdot}59$.

Behaviour of Triethylphosphine with Sulphuretted Hydrogen.—The phosphorus-base has no action on *sulphuretted hydrogen.*

When it is brought in contact with hydrosulphuric acid over mercury, the gas does not exhibit any alteration. No sulphide of triethylphosphine is formed, even in presence of air, as might indeed have been expected. The attraction of the phosphorus-base for oxygen prevents the oxidation of the sulphuretted hydrogen; a solution of this gas in water, when mixed with a few drops of triethylphosphine, may be preserved in air-filled vessels much longer than without this addition.

Behaviour of Triethylphosphine with Sulphide of Nitrogen.—*Sulphide of Nitrogen*, N S, prepared as recommended by Fordos and Gelis, viz., by the action of ammonia on chloride of sulphur dissolved in disulphide of carbon, is decomposed by triethylphosphine, with evolution of light and heat. Gas is evolved, and at the same time a yellowish liquid is produced, which, on cooling, solidifies into a fibrous mass of crystals of the sulphide.

Behaviour of Triethylphosphine with Mercaptan.—When these two bodies are mixed together in an atmosphere of carbonic acid, no alteration takes place, even if they are left in contact for some time, or if they are heated to 100° in sealed tubes for twenty-four hours. But if the mixture be poured into an air-filled flask, crystals of sulphide of triethylphosphine make their appearance in a few hours. The crystals increase if the air has free access to the mixture; but if the flask be corked, the crystallization is interrupted. On opening the flask, the entry of the air may be recognized by the light cloud which the phosphorus-base, diffused through the atmosphere of the vessel, forms with the oxygen. When a mixture containing excess of mercaptan was left for a few days in an open flask, every trace of phosphorus-base had disappeared, and the remaining colourless liquid was filled with crystals of the sulphide. On mixing this liquid with water, it separated into two layers, the upper of which quickly solidified, especially on exposure to the air, to an imperfectly crystalline mass, easily recognized as a mixture of sulphide of triethylphosphine with excess of mercaptan. The impure crystals were exposed for a while to the air and then recrystallized from boiling water, when, on analysis, they gave results agreeing with the formula

$$C_6H_{15}PS = (C_2H_5)_3PS.$$

The lower stratum of liquid is aqueous alcohol containing small quantities of oxide of triethylphosphine and mercaptan. To remove the latter, the liquid was shaken up with recently precipitated mercuric oxide and distilled. The distillate, rectified several times over lime, yielded a clear liquid, which burnt with a colourless flame and exhibited all the characters of alcohol.

The interpretation of this result appears at the first glance exceedingly simple; the sulphide of triethylphosphine cannot be formed directly from the phosphorus-base, but owes its origin to the oxide first produced by the action of air, this oxide being decomposed by the mercaptan and yielding sulphide of triethylphosphine and alcohol:

$$(C_2H_5)_3PO + \left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\} S = \left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\} O + (C_2H_5)_3PS.$$

Experiment shows, however, that this equation illustrates only the final result of the reaction. Oxide of triethylphosphine and mercaptan, brought together under the most various conditions at ordinary temperatures and under pressure, do not yield a trace of sulphide of triethylphosphine; and we have to suppose, therefore, that the mercaptan interchanges its sulphur with the oxygen of the oxide of triethylphosphine, only at the instant of formation of the latter, or what comes to the same thing, that the oxygen of the air, in presence of a substance so greedy of sulphur as triethylphosphine, directly takes the place of the sulphur in the mercaptan.

In connection with this subject, various attempts were made to replace the oxygen in oxide of triethylphosphine by sulphur. But neither by treatment with sulphide of ammonium, nor by continued boiling with the higher sulphides of potassium, could the oxide be converted into the corresponding sulphide, whereas the conversion of the sulphide into the oxide takes place without any difficulty. This, however, is not more than might have been expected from the behaviour of the oxide with hydrochloric acid, mentioned in one of the preceding paragraphs. The different degrees of stability which characterize the oxide and the sulphide of triethylphosphine may also be strikingly seen in the behaviour of these compounds with sodium, the sulphide being reduced, with the greatest facility, to free triethylphosphine, even below the melting-point of the sodium, whereas the oxide may be distilled

from sodium without experiencing the slightest alteration.* Ebullition with ordinary concentrated nitric acid likewise converts the sulphide into the oxide, the sulphur being at the same time transformed into sulphuric acid. The liquid filtered off from the precipitate obtained by barium-salts, when evaporated to dryness and fused with nitrate of potassium, yields no further trace of sulphur.

Behaviour of Triethylphosphine with Disulphide of Carbon.— These two bodies, when mixed in the anhydrous state, act upon one another with considerable force, amounting frequently to explosive violence, and unite into a red crystalline mass. The compound is best prepared by mixing the solutions of its constituents in alcohol or ether: the new body then instantly separates in beautiful red crystalline laminæ.

Several times recrystallized from alcohol and dried over sulphuric acid, the new body has furnished results leading to the formula,

$$C_7 H_{15} PS_2 = (C_2H_5)_3 P + CS_2.$$

The red crystals are not the only product of the action of disulphide of carbon on triethylphosphine. A second beautifully crystallized compound is deposited after some time from the mother-liquor. This substance is formed in extremely minute quantity: its nature is not yet established.

The compound of triethylphosphine with disulphide of carbon is insoluble in water, sparingly soluble in ether, moderately soluble in disulphide of carbon, and somewhat more soluble in alcohol, especially when heated. The solution has no action on vegetable colours. From the boiling alcoholic solution, it separates on coolin red needles, somewhat resembling the crystals of chromic acid, which are formed by the action of strong sulphuric acid on a solution of chromate of potassium. The ethereal solution, left to evaporate in an open cylinder, deposits finely developed, deep-red crystals of considerable size. Quintino Sella has examined these crystals with the following results.

* In the previous memoir, it is stated that the phosphorus-base is reproduced from the oxide by the action of metallic sodium. Probably the oxide used in the former experiments contained a small quantity of free triethylphosphine, and thus led to an erroneous statement.

"System monoclinic :—

100, 101 = 29° 41½′ ; 010, 111 = 74° 4′ ; 101, 001 = 27° 7½′.

Forms observed :—

100, 010, 001, 110, $\bar{1}01$ (Fig. 15.)

Combinations observed :—

100, 110, 001, $\bar{1}01$ (Fig. 16.)
100, 110, 001, $\bar{1}01$, 010 (Fig. 17.)

Fig. 15.

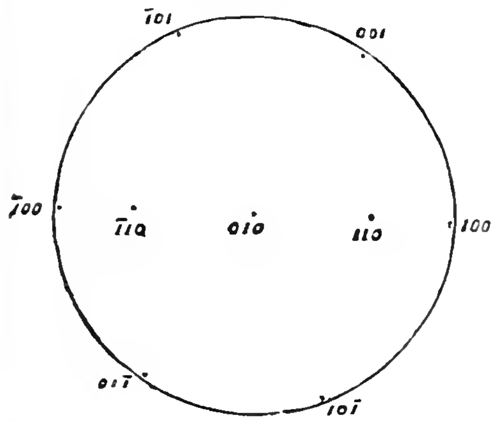


Fig. 16.

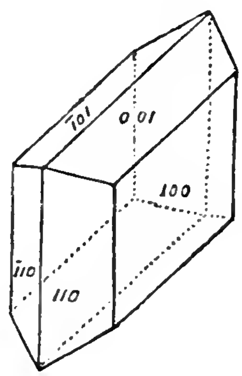
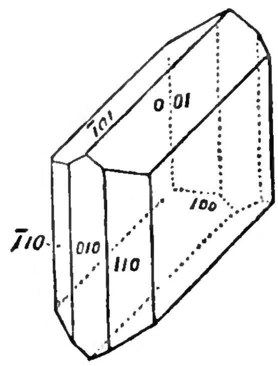


Fig. 17.



Cleavages :—010, 100, neat and easy.

The crystals are optically positive : the medium-line coincides with the axis of symmetry [010]. The interior angle of the optical axes is not very different from 70°. The plane of the optical axes is nearly parallel to the face 001. The axis of symmetry, or of smallest elasticity, exhibits a violet-red colour, which even in very thin layers is very intense. The axis nearly parallel to [100], or the axis of greatest elasticity, exhibits a similar but much lighter red tint. The normal shows in thin layers a straw-yellow, in thicker layers an orange-yellow colour. In polarized light, one of the most beautiful examples of dichroism is observed by looking across the faces 010, the colour passing in the case of thin layers from a pure yellow to a deep red. But even in ordinary light the dichroism is perceptible ; for the light passes with a violet-red across the faces 100, and with an orange-red colour of far less intensity across the faces 010.

Hardness less than that of gypsum."

The red crystals appear to possess the character of a weak base. They dissolve in strong hydrochloric acid, forming a colourless liquid, from which potassa or ammonia throws down the compound in its original state, though somewhat lighter in colour, on

account of its minute state of division. The acid solution forms with dichloride of platinum a light yellow amorphous salt, insoluble in alcohol and ether, which changes colour and somewhat decomposes on drying. It darkens in colour, even when dried *in vacuo*, hydrochloric acid fumes being evolved. The analysis of a slightly decomposed salt gave results approximately agreeing with the formula,

$$(C_2 H_5)_3 P, CS_2, H Cl, PtCl_2.$$

The gold-salt is obtained like the platinum-salt, and exhibits similar properties.

It is not very easy to form a clear notion of the constitution of the red crystals. According to the formula, the compound is the primary triethylphosphonium-salt of sulphocarbonic acid *minus* 1 equiv. of sulphuretted hydrogen, and corresponds therefore to sulphocarbamic acid, the ammonium salt of which, as is well known, is produced by the action of ammonia on disulphide of carbon. There is, however, no analogy in the constitution of the two substances.

The red crystals exhibit a remarkable tendency to pass into the sulphide of triethylphosphine. On mixing their alcoholic solution with oxide or nitrate of silver, carbonic acid is evolved, sulphide of silver and metallic silver are separated, and the filtered solution, when evaporated, deposits crystals of the sulphide:

$$(C_2 H_5)_3 P, CS_2 + 2Ag_2 O = Ag_2 S + Ag_2 + CO_2 + (C_2H_5)_3 PS.$$

The disulphide-of-carbon-compound undergoes a similar change, even under the influence of moisture. Crystals which had not been dried with sufficient care, were changed, after a few months, when kept in corked tubes, into a yellowish white, semifluid mass, of peculiar odour, which, by recrystallization from boiling water, furnished a considerable quantity of pure sulphide of triethylphosphine. To establish this transformation by numbers, the purified crystals were identified by analysis.

It is obvious that the transformation of the red crystals into the sulphide involves the co-operation of the elements of water. Perfectly dry crystals were preserved in sealed tubes for many months without the slightest alteration. The crystals fuse at 95° and volatilize at 100°; in the absence of moisture, they may be heated

under pressure to 150° without undergoing any decomposition. The phenomena are very different in the presence of water. When exposed for some days in sealed tubes with water to a temperature of 100°, the red crystals are gradually transformed into white needles, which are easily recognized as sulphide of triethylphosphine. The transformation is independent of atmospheric air: for it takes place with equal facility in vessels with air, or carbonic acid, or *in vacuo*.

The products which accompany the sulphide formed in this reaction vary according to the time during which the red crystals are digested with water. If the tubes be allowed to cool after one or two days' digestion, the liquid generally becomes filled with white needles, which are, however, still intermixed with red prisms, showing that the transformation is not yet complete. Scarcely any gas escapes when the tubes are opened, but when gently heated, the liquid yields abundance of disulphide of carbon. On the other hand, when the tubes are heated until the transformation of the red compound is accomplished,—which generally takes place after three or four days' digestion,—a large volume of gas escapes on opening the tubes, and they are occasionally shattered. The gas which is thus evolved consists of sulphuretted hydrogen and carbonic acid, which are obviously secondary products of the reaction, arising from the protracted action of the water upon the disulphide of carbon, which is separated in the first stage of the process. The liquid from which the crystals of sulphide have been deposited has a distinctly alkaline reaction, which belongs neither to the sulphide nor to the red crystals from which the sulphide arises, both these compounds being without action on vegetable colours. To seize the basic substance, the liquid was evaporated on the water-bath, till the sulphide had been as far as possible expelled, and then precipitated with iodide of zinc, which does not combine with the sulphide, traces of this body which might have remained, being in this manner eliminated. The iodide-of-zinc-precipitate was semisolid, and slowly became crystalline on treatment with alcohol; it did not, however, exhibit a sufficiently definite appearance to warrant its analysis. The bases were therefore at once liberated again by digesting the precipitate with oxide of silver; the powerfully alkaline liquid thus obtained gave, on addition of hydrochloric acid and dichloride of platinum, a difficultly soluble platinum-salt, crystallizing, after the necessary purification,

from boiling water, in splendid octohedra, which on analysis proved to be the methyl-triethylphosphonium-compound.

The solution filtered off from the octohedral salt gave, on evaporation, the extremely soluble six-sided tables of the platinum-salt of oxide of triethylphosphine, which I have mentioned in the commencement of this paper.

The products of the action of water upon the red crystals, then, are sulphide of triethylphosphine—the principal product—oxide of triethylphosphine, hydrate of methyl-triethylphosphonium, and disulphide of carbon, which may be partly or entirely converted into sulphuretted hydrogen and carbonic acid. Four molecules of the disulphide-of-carbon-compound and two molecules of water contain the elements of two molecules of the sulphide, one molecule of the oxide, one molecule of the hydrated phosphonium, and three molecules of disulphide of carbon:

$$4[(C_2H_5)_3P{\cdot}CS_2] + 2\left[\left.\begin{matrix}H\\H\end{matrix}\right\} O\right] = 2[(C_2H_5)_3PS] + (C_2H_5)_3PO + \left.\begin{matrix}[(CH_3)(C_2H_5)_3P]\\H\end{matrix}\right\} O + 3CS_2.$$

Whilst engaged with the experiments involved in the elucidation of this subject, I observed occasionally small well-defined yellow crystals disseminated among the mixture of white and red needles, which are deposited when the digestion-tubes are allowed to cool, before the transformation is terminated. The yellow crystals appeared in greater quantity towards the close of the operation, and were found to be a secondary product formed by the action of the sulphuretted hydrogen, which is generated in the last stage of the process. I have since learnt to prepare the yellow crystals by a simpler and more definite method. This remarkable compound has become the starting-point of a new enquiry, the result of which I reserve for a later communication.

The formation of the red crystals by the union of triethylphosphine and disulphide of carbon takes place so rapidly, and with such facility, that ever since the first time I observed this phenomenon, I have used the disulphide of carbon as a reagent for the detection of the phosphorus-bases: for trimethylphosphine exhibits a deportment perfectly similar to that of the ethyl-body. The minutest quantities of these bases may thus be readily and

safely recognized. The reaction is best observed by pouring the liquid to be examined upon a watch-glass, and allowing the vapour of the disulphide of carbon to flow from an inclined bottle upon the liquid. The watch-glass immediately becomes coated with a beautiful net-work of the red crystals. It requires scarcely to be mentioned that the crystals are formed only when the phosphorus-bases are free. They appear, however, readily on adding to a mixture of their salts and disulphide of carbon, a drop of potash, which liberates the bases.

On the other hand, triethylphosphine may be employed with the greatest advantage as a test for disulphide of carbon. There is, in fact, no test for this substance, which in delicacy could be compared with it. By its aid the presence of the disulphide in the most volatile fractions of coal-tar-benzol is readily proved; even the exceedingly small quantity of disulphide of carbon diffused in the most carefully purified coal-gas may, as I have shown already in another place,* be recognized without any difficulty.

In order to satisfy myself that disulphide of carbon may be employed with safety as a test for the phosphorus-bases, it was necessary to examine the deportment of this compound with the *arsines* and *stibines*. Disulphide of carbon exhibits no reaction with *triethylarsine* and *triethylstibine*. I have left mixtures of these bases with the disulphide in contact for a considerable length of time, both at the common temperature and at 100°, without being able to observe the slightest alteration. I have also satisfied myself that disulphide of carbon, at all events in the common temperature, is without action upon *phosphoretted hydrogen*.

In examining somewhat minutely into the deportment of triethylphosphine with sulphur-compounds, the organic sulphocyanates could not be left unnoticed. My attention was in the first place fixed by the sulphocyanate of phenyl, which I had just discovered at the time I was engaged in the study of these reactions.

Action of Sulphocyanate of Phenyl upon Triethylphosphine. The reaction between the two substances in the anhydrous state is very

* Quarterly Journal of the Chemical Society, vol. xiii., p. 87.

violent, and frequently causes the inflammation of the phosphorus-base. The mixture assumes a deep-yellow colour, and on cooling deposits sometimes splendid uranium-yellow needles; often, however, it remains liquid for hours, and even for days, but suddenly solidifies, when touched with a glass rod, into a hard yellow crystalline mass. The new compound is most conveniently prepared by allowing the sulphocyanate to act upon the triethylphosphine in the presence of a considerable volume of ether. The product of the reaction, being difficultly soluble in cold ether, often separates in the crystalline state, more frequently as an oil, which solidifies after some time. In order to ensure perfect purity, it is only necessary to crystallize the compound once or twice from boiling ether.

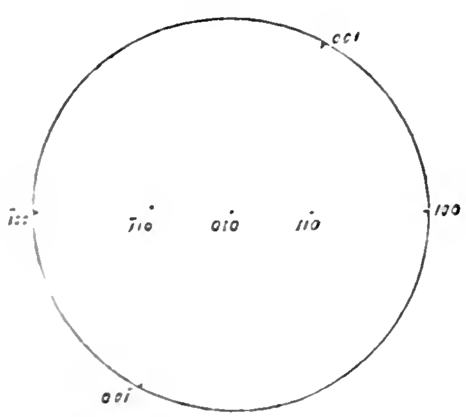
The numbers obtained in analysis characterize the new body as a combination of one molecule of triethylphosphine with one molecule of sulphocyanate of phenyl:

$$\left.\begin{matrix} C_2H_5 \\ C_2H_5 \\ C_2H_5 \end{matrix}\right\} P + \left.\begin{matrix} CN \\ C_6H_5 \end{matrix}\right\} S = C_{13}H_{20}NPS.$$

The above formula is fully corroborated by the analysis of several well-defined salts, which will be mentioned presently.

The yellow crystals are insoluble in water. Alcohol, both cold and hot, dissolves them in almost every proportion. The best crystals were obtained by the spontaneous evaporation of the ethereal solution in high open cylinders. Some of these crystals were so well developed, that Quintino Sella was enabled to submit them to a detailed crystallographic examination, an abstract of which I here insert.

Fig. 18.



"System monoclinic:—

100, 001 = 61° 2′; 010, 110 = 44° 27′.

Forms observed:—

100, 010, 001, 110 (Fig. 18).

Combinations observed:—

110, 001 (Fig. 19).
110, 100, 001 (Fig. 20).
110, 001; 100, 010 (Fig. 21).

Fig. 19.

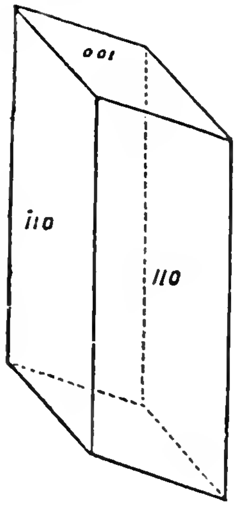


Fig. 20.

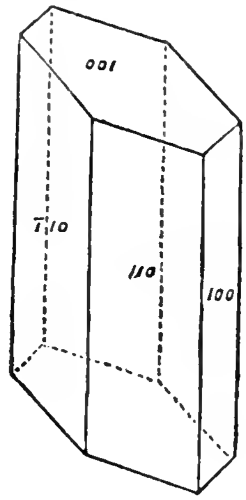
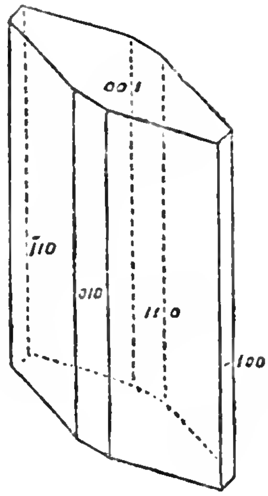


Fig. 21.



Cleavage 100 easy; cleavage 110 fibrous.

Hardness nearly that of gypsum.

If we endeavour to associate this compound with well-known bodies, in order to obtain some insight into the probable arrangement of its proximate constituents, both its formation and its deportment point to *urea*. Urea is generated by the combination of ammonia and cyanic acid; the yellow crystals are formed by the union of two compounds derived respectively from ammonia and cyanic acid. In urea the faculty possessed by ammonia of combining with acids has been preserved; the new compound likewise exhibits the sharply defined characters of a monacid base. Whatever constitution be attributed to urea, must also be claimed for the new base. If urea be viewed as a monacid diamine,

$$CH_4N_2O = \left.\begin{matrix}(CO)''\\ H_2\\ H_2\end{matrix}\right\}N_2,$$

the yellow crystals present themselves as

$$C_{13}H_{20}NPS = \left.\begin{matrix}(CS)''\\ (C_2H_5)_2\\ (C_2H_5)(C_6H_5)\end{matrix}\right\}NP.$$

The new compound accordingly belongs to the type urea: it may be viewed as ordinary urea, the oxygen of which is replaced by sulphur, and the hydrogen by ethyl and phenyl, whilst phosphorus has taken the place of half the nitrogen. Regarded from this point of view, the formation of the new compound presents considerable interest: it offers the first example of

the perfect substitution of the hydrogen in urea, which had remained doubtful hitherto, and illustrates in a remarkable manner the persistence of the type urea under the influence of an almost overwhelming substitution. At the same time it deserves to be noticed that the corresponding oxygenated urea remains to be discovered.

The new compound, as already mentioned, possesses the properties of a well-defined organic base. Insoluble in water, it dissolves with the greatest facility even in very diluted acids, giving rise in many cases to easily-crystallizable salts which are capable of double decomposition, and from which the base may be reprecipitated by the careful addition of potassa or ammonia.

Chloride.—The solution of the phenyl-compound in warm concentrated hydrochloric acid solidifies on cooling to a crystalline mass, which, when recrystallized from moderately warm water, furnishes splendid cadmium-yellow crystals, frequently an inch in length. Boiling water has to be avoided, since it decomposes the substance. Even the dry crystals are altered at 100°; they must therefore, like all the other salts of the base, be dried *in vacuo* over sulphuric acid.

The chloride is composed according to the formula

$$C_{13}H_{21}NPSCl = \left[\left.\begin{matrix}(CS)'' \\ H(C_2H_5)_2 \\ (C_2H_5)(C_6H_5)\end{matrix}\right\} NP\right] Cl.$$

Bromide.—Both in preparation and properities, precisely similar to the salt previously mentioned. It contains

$$C_{13}H_{21}NPSBr = \left[\left.\begin{matrix}(CS)'' \\ H(C_2H_5)_2 \\ (C_2H_5)(C_6H_5)\end{matrix}\right\} NP\right] Br.$$

Platinum-salt.—The solution of the chloride furnishes with dichloride of platinum a light-yellow crystalline precipitate. Dilute solutions slowly deposit this salt in somewhat better-formed crystals, which are frequently grouped in lily-shaped aggregations. It was found to contain

$$C_{13}H_{21}NPSPtCl_3 = \left[\left.\begin{matrix}(CS)'' \\ H(C_2H_5)_2 \\ (C_2H_5)(C_6H_5)\end{matrix}\right\} NP\right] Cl, PtCl_2.$$

I did not succeed in preparing the sulphate or the nitrate of the base. The phenyl-compound is rapidly decomposed under the influence of these acids; it forms, however, beautifully crystallized salts with the iodides of methyl and ethyl. I have examined only the former of these compounds.

Iodide-of-Methyl-compound.—When iodide of methyl is poured into an ethereal solution of the urea, the new compound is at once separated as a heavy oil which rapidly solidifies into a crystalline mass. The crystals dissolve in boiling water which on cooling deposits the iodide in splendid needles of a golden-yellow colour.

These crystals contain

$$C_{14}H_{23}NPSI = \left[\left.\begin{matrix}(CS)'' \\ (CH_3)(C_2H_5)_2 \\ (C_2H_5)(C_6H_5)\end{matrix}\right\} NP\right] I.$$

Platinum-salt of the Methyl-compound.—The chloride obtained by treating the iodide with chloride of silver, yields on addition of dichloride of platinum, an acicular platinum-salt, which may be recrystallized without decomposition from boiling water. Its composition corresponds to that of the iodide:

$$C_{14}H_{23}NPSPtCl_3 = \left[\left.\begin{matrix}(CS)'' \\ (CH_3)(C_2H_5)_2 \\ (C_2H_5)(C_6H_5)\end{matrix}\right\} NP\right] Cl, PtCl_2.$$

The iodide, when treated with oxide of silver, furnishes, together with iodide of silver, a very caustic liquid containing the corresponding oxide. The presence in this liquid of the compound,

$$C_{14}H_{24}NPSO = \left.\begin{matrix}[(CH_3)\{(CS)''(C_2H_5)_3(C_6H_5)NP]\} \\ H\end{matrix}\right\} O,$$

is proved by the fact of the characteristic needle-shaped platinum-salt being immediately reproduced when it is saturated with hydrochloric acid and mixed with dichloride of platinum. The free base is, however, readily decomposed. On boiling, the odour of sulphocyanate of phenyl becomes at once perceptible; if ebullition be continued until the odour has disappeared, addition of hydrochloric acid and dichloride of platinum no longer furnishes the difficulty soluble needles. In their place, large well-developed orange-yellow octahedra are deposited on evaporation, which by analysis were found to be the platinum-salt of methyl-triethyl-phosphonium.

The free methylated phenyl-base then simply splits, by ebullition, into sulphocyanate of phenyl and oxide of methyl-triethylphosphonium. When the solution is boiled by itself, the sulphocyanate is separated as such; when it is boiled in the presence of oxide of silver, the sulphocyanate is, partly at least, destroyed, the alkaline solution becoming acid and exhibiting the presence of considerable quantities of sulphuric acid. This transformation clearly shows how feebly the proximate constituents are held together in the urea. The same instability is perceptible in the general deportment of the compound. Even extremely dilute nitric acid liberates the sulphocyanate of phenyl, whilst the phosphorus-base is converted into the oxide. The chloride is one of the more stable salts of the urea, but it is likewise readily altered: on addition of a large quantity of water, the solution of the salt becomes milky, the sulphocyanate of phenyl being separated in oily globules, and now contains the chloride of triethylphosphonium. On adding ammonia to the *concentrated* solution of the chloride, the urea, as already stated, is separated without change, and may be easily recovered by taking up with ether and crystallizing. If, on the other hand, the *dilute* solution be boiled with ammonia, the turbidity perceptible in the commencement disappears again, and after a few moments beautiful crystals of *phenyl-sulphocarbamide* are deposited, triethylphosphine being simultaneously liberated:

$$\left.\begin{matrix}(CS)'' \\ (C_2H_5)_3 \\ (C_6H_5)\end{matrix}\right\} NP + H_3N = (C_2H_5)_3P + \left.\begin{matrix}(CS)'' \\ (C_6H_5) \\ H_3\end{matrix}\right\} N_2.$$

On treating the chloride with potassa, phenomena exactly analogous are observed; the crystals which are separated, are, however, *diphenyl-sulphocarbamide*:

$$2\left[\left.\begin{matrix}(CS)'' \\ (C_2H_5)_3 \\ (C_6H_5)\end{matrix}\right\} NP\right] + 4\left[\left.\begin{matrix}K \\ H\end{matrix}\right\} O\right] = \left.\begin{matrix}K \\ K\end{matrix}\right\} S + \left.\begin{matrix}K \\ K\end{matrix}\right\} CO_3 + \left.\begin{matrix}H \\ H\end{matrix}\right\} O$$

$$+ 2[(C_2H_5)_3P] + \left.\begin{matrix}(CS)'' \\ (C_6H_5)_2 \\ H_2\end{matrix}\right\} N_2.$$

If a few drops of disulphide of carbon be added to the solution of the urea, the liquid, when gently heated, assumes a deep red

colour, and deposits on cooling the beautiful ruby-red crystals $(C_2H_5)_3P,CS_2$, which I have mentioned in a previous paragraph of this paper. The mother-liquor of these crystals furnishes on evaporation oily droplets of sulphocyanate of phenyl. The urea, even when perfectly pure and dry, cannot be preserved without undergoing a gradual alteration. If the crystals be left under a bell-jar containing atmospheric air, they become dull, and at last moist and sticky, whilst a peculiar extremely disagreeable odour, distantly resembling that of hydrocyanic acid, becomes perceptible; at the same time, a delicate net-work of fine needles begins to appear on the glass, easily recognized as sulphide of triethylphosphine. The crystals of the urea fuse at 57°·5, forming a yellow liquid, which, in consequence of incipient decomposition, resolidifies but slowly and imperfectly. At 100°, the phenomena just mentioned are much more distinctly observed, and especially the smelling body is unmistakeably perceived. The peculiar smelling body is likewise almost overwhelmingly produced on evaporating the ethereal mother-liquor of the compound. As yet I have not been able to lay hold of the possessor of this remarkable odour. The ethereal mother-liquor, when evaporated, leaves a brown syrup, which after some time deposits large crystals of sulphide of triethylphosphine. Submitted to distillation, this residue yields, together with other products, an additional quantity of the crystallized sulphur-compound.

Transformations precisely similar are observed when the crystals of the urea, in sealed tubes, are exposed to a temperature of from 150° to 160°. The brown fused mass which is thus formed, solidifies on cooling with crystalline structure; the crystals, however, are no longer the original compound, but sulphide of triethylphosphine, which is surrounded by another substance. The examination of this reaction has not yet been completed. The nature of the final product of the metamorphosis may, however, be anticipated, in some measure, by the results obtained in studying the deportment of triethylphosphine with *sulphocyanate of ethyl* and *sulphocyanate of ethylene*, which will be briefly mentioned in some of the following paragraphs.

Action of Sulphocyanate of Allyl upon Triethylphosphine.—To generalize the relations established in the preceding paragraph, I

was induced to examine the deportment of the phosphorus-base with oil of mustard. The two bodies act upon each other with extraordinary violence; the mixture turns brown, but does not solidify either by cooling or by agitation. After some days, however, the syrup yields brown crystals which are difficult to purify. The purification of the compound succeeds, however, without any difficulty when the reaction is allowed to take place in ether. In this manner a crystalline mass is easily obtained, which requires only to be washed with cold ether, and then once recrystallized from boiling ether.

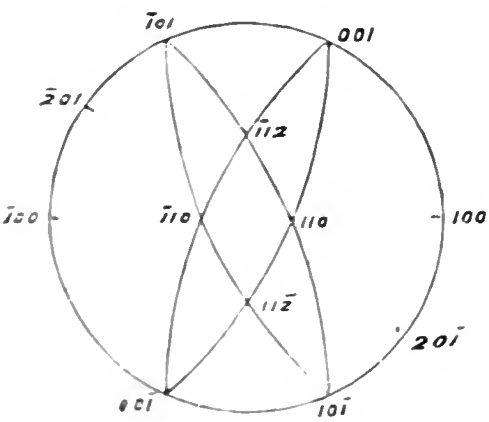
It has the formula,

$$C_{10}H_{20}NPS = \left.\begin{matrix}(CS)'' \\ (C_2H_5)_2 \\ (C_2H_5)(C_3H_5)\end{matrix}\right\} NP.$$

The allyl-compound behaves in all respects like the phenyl-compound. It is insoluble in water, but easily soluble in alcohol; the solution has a faintly alkaline reaction. It fuses at 68° and solidifies at 61°. At a higher temperature, it is decomposed exactly like the phenyl-compound. In this case also, a peculiar, and if possible, still more repulsive odour is evolved, while crystals of sulphide of triethylphosphine separate in large quantity.

The allyl-compound crystallizes with extraordinary facility. There is no difficulty in obtaining it in colourless transparent crystals half an inch in length, and perfectly developed on all sides. I scarcely remember any other organic compound that crystallizes so readily. The crystals, as appears from the measurements of Quintino Sella, are isomorphous with those of the phenyl-compound. Sella has communicated to me the following details respecting his examination.

Fig. 22.



" System monoclinic :—

$100, 101 = 35° 42'$; $001, 101 = 29° 3'$;
$010, 111 = 39° 22'$.

Forms observed :—

$100, 001, 110, \bar{1}01, \bar{2}01, \bar{1}12$ (Fig. 22).

Combinations observed:—

001, 100, 110 (Fig. 23).

001, $\bar{1}01$, 110 (Fig. 24).

100, 001, $\bar{1}01$, 110 (Fig. 25).

100, 001, $\bar{1}01$, 110, $\bar{1}12$ (Fig. 26).

100, 001, $\bar{1}01$, 110, $\bar{2}01$, $\bar{1}12$ (Fig. 27).

Fig. 23.

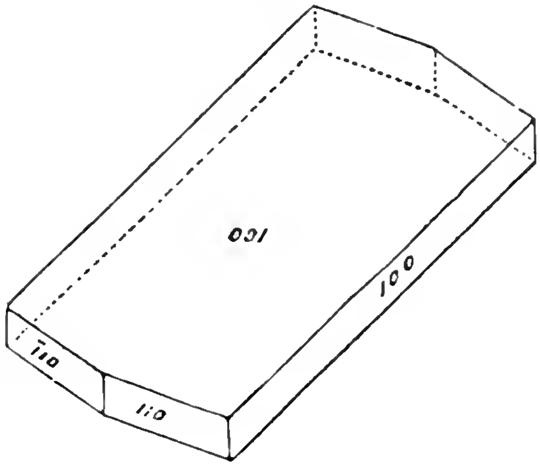


Fig. 24.

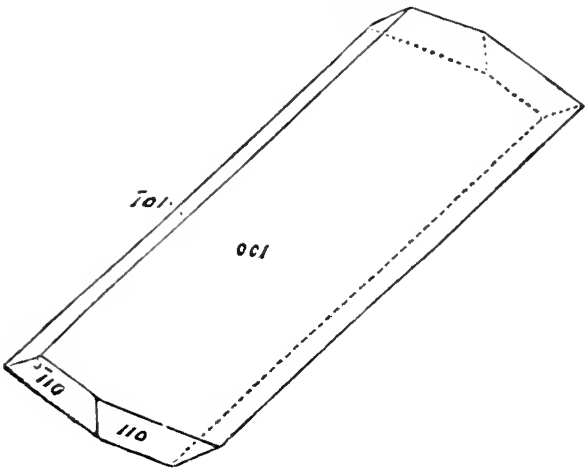
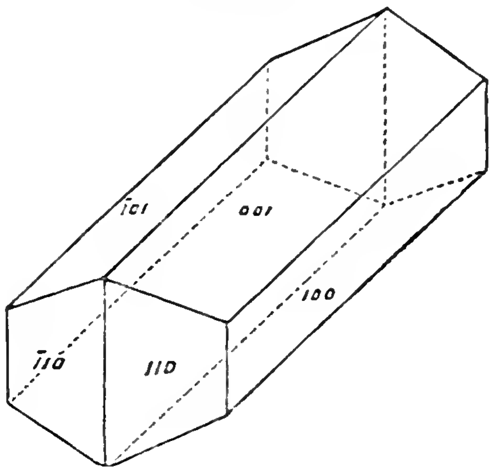


Fig. 25.



The form $\bar{1}12$ is sometimes hemihedral.
Cleavages 100 and 001 neat, easy.

Fig. 26.

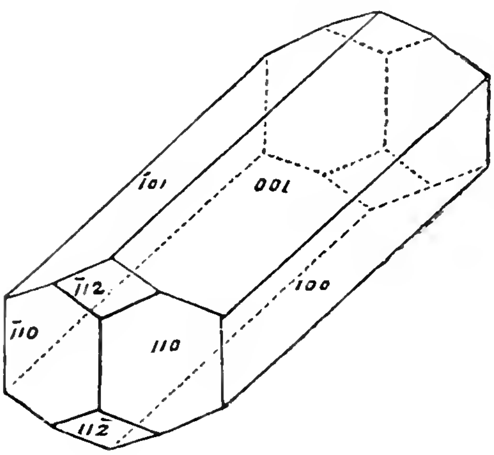
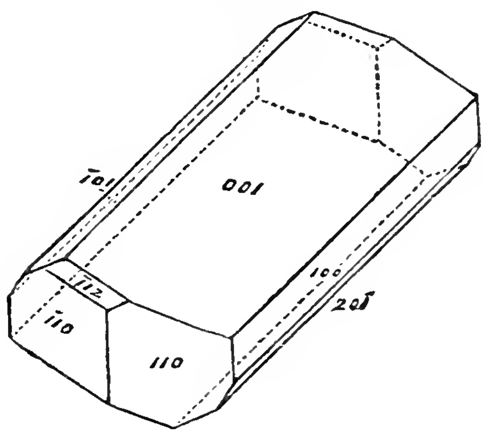


Fig. 27.



The optical axes are situated in the plane of symmetry, viz., 010; their principal medium is perpendicular to $\bar{1}01$, and their internal angle is about $72\frac{1}{2}°$. The index of refraction of the ray vibrating parallel to the axis of symmetry is $\beta = 1{\cdot}657$.

Hardness less than that of gypsum."

Platinum-salt.—I have contented myself with verifying the formula of the allyl-urea by the analysis of the platinum-salt. The allyl-compound dissolves readily in hydrochloric acid, and the solution, when mixed with dichloride of platinum, yields a light-yellow scaly precipitate having a silky lustre, which fuses to a yellow oil in boiling water, and is represented by the formula—

$$C_{10}H_{21}NPSPtCl_3 = \left[\left.\begin{matrix}(CS)'' \\ H(C_2H_5)_2 \\ (C_2H_5)(C_3H_5)\end{matrix}\right\} NP\right] Cl, PtCl_2.$$

The allyl-base described in the preceding pages has the composition of sulphocyanide of triethyl-allylphosphonium.

$$\left.\begin{matrix}(CS)'' \\ (C_2H_5)_2 \\ (C_2H_5)(C_3H_5)\end{matrix}\right\} NP = \left.\begin{matrix}CN \\ [(C_2H_5)_3(C_3H_5)P]\end{matrix}\right\} S.$$

I felt some interest in comparing the latter compound with the allyl-base. Iodide of allyl acts with the greatest energy upon triethylphosphine. The solid product of the reaction, recrystallized from alcohol, furnishes splendid needles of iodide of triethyl-allylphosphonium, which, by analysis, was found to contain—

$$[(C_2H_5)_3(C_3H_5)P]I.$$

Treatment with chloride and oxide of silver yields the corresponding chloride and hydrate. They resemble in every respect the tetrethylphosphonium-compounds. The chloride gives with dichloride of platinum an easily crystallizable octohedral platinum-salt.

The hydrate of triethyl-allylphosphonium forms with hydrosulphocyanic acid a difficultly crystallizable salt which is easily soluble in water, and differs, as might have been expected, entirely from the allyl-base which has the same composition.

Behaviour of Triethylphosphine with the Sulphocyanates of Ethyl and Ethylene.—I have in vain endeavoured to produce, by the action of triethylphosphine on the sulphocyanates of methyl, ethyl, and amyl, compound ureas analogous to the allyl- and phenyl-bodies. It is true that these substances act upon triethylphosphine even at ordinary temperatures; in the case of sulphocyanate of

methyl, indeed, the action is very brisk, but I did not succeed in obtaining definite compounds. Sulphocyanate of ethyl remained for months in contact with triethylphosphine without depositing any crystalline compound. The non-production of these ureas cannot, however, excite surprise, if we remember in how many respects, and especially in the relation to ammonia, the sulphocyanogen-compounds of ethyl and its homologues differ from those of allyl and phenyl.

When a mixture of triethylphosphine and one of the above-mentioned sulphocyanates is heated for some hours in a sealed tube to 100°, an abundant crop of crystals of sulphide of triethylphosphine is deposited from the liquid. These crystals are surrounded by a brown viscid substance, soluble to a certain extent in water, easily soluble with green colour in alcohol. In order to disentangle from this mixture the complementary product of the reaction, the liquor was shaken with ether to separate the sulphide, evaporated with an excess of hydrochloric acid, and the residue redissolved in water, when a quantity of the brown impurities remained insoluble. The filtered solution gave with trichloride of gold a dingy yellow precipitate, which, by treatment with sulphuretted hydrogen, reprecipitation of the separated chloride by trichloride of gold, &c., ultimately assumed the characters of the pure gold-salt of triethylphosphonium which was identified by analysis. The beautifully orange-yellow platinum-salt was likewise analysed.

The action of sulphocyanate of ethyl upon triethylphosphine may be accordingly represented by the equation:

$$\left.\begin{matrix} CN \\ C_2H_5 \end{matrix}\right\} S + 2[(C_2H_5)_3P] + \left.\begin{matrix} H \\ H \end{matrix}\right\} O = (C_2H_5)_3PS + \left.\begin{matrix} [(C_2H_5)_4P] \\ H \end{matrix}\right\} O + HCN.$$

I have not been able to trace directly the hydrocyanic acid which figures in this equation, but this acid appears unmistakeably in its products of decomposition. The brown substance, which accompanies the sulphide of triethylphosphine and the hydrate of tetrethylphosphonium, is rich in nitrogen: boiled for some time with hydrochloric acid, it yields abundance of chloride of ammonium.

I have likewise examined the behaviour of disulphocyanate of

ethylene with triethylphosphine. The reaction takes place with energy at ordinary temperatures. When triethylphosphine is poured into a concentrated alcoholic solution of sulphocyanate of ethylene, the liquid immediately solidifies to a dazzling white crystalline mass of sulphide of triethylphosphine. It deserves to be noticed that the same decomposition takes place also when the substances are allowed to react in presence of anhydrous ether. The transformation which the sulphocyanate of ethylene undergoes under the influence of triethylphosphine is perfectly analogous to the change of the ethyl-compound when submitted to the same agent. Instead of a derivative of tetrethylphosphonium, the sulphocyanate of ethylene produces the cyanide of a diatomic metal, of *ethylene-hexethyl-diphosphonium*:

$$\underbrace{\left.\begin{matrix}(CN)_2\\(C_2H_4)''\end{matrix}\right\}S_2}_{\text{Sulphocyanate of ethylene.}} + 4\underbrace{[(C_2H_5)_3P]}_{\text{Triethylphosphine.}} = 2\underbrace{[(C_2H_5)_3PS]}_{\text{Sulphide of triethylphosphine.}} +$$

$$\underbrace{\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''C_2N.}_{\text{Dicyanide of ethylene-hexethyl-diphosphonium.}}$$

Owing to the low temperature at which the reaction is accomplished, the hydrocyanic acid is not changed in this case, and may be recognised without difficulty by the ordinary reagents. The diphosphonium, which is simultaneously formed, was traced as platinum-salt, exactly in the same manner as the tetrethylphosphonium in the process previously mentioned. The product of the reaction, freed as far as possible from the sulphide by repeated evaporation and ultimately by treatment with ether, was precipitated by dichloride of platinum. The dingy platinum-salt was purified by treatment with sulphuretted hydrogen and reprecipitation. Repeatedly treated in this manner, it assumed the character of a pure compound, which on analysis gave numbers closely agreeing with the formula,

$$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2,\ 2PtCl_2.$$

Since I shall have to give a detailed account of the diphosphonium-compounds in one of the following sections of this inquiry, I

need not for the present enter into further particulars regarding this reaction.

In concluding this paragraph, I may append a few remarks upon the deportment of sulphocyanate of triethylphosphonium under the influence of heat. This salt is readily procured by dissolving triethylphosphine in hydrosulphocyanic acid. Submitted to the action of heat, it is partly volatilized without decomposition: the greater portion, however, is decomposed, sulphide and the disulphide-of-carbon-compound of triethylphosphine, together with free disulphide of carbon, appearing among the volatile products of the reaction, while a brown ill-defined substance remains in the retort, yielding when treated with an alkali, an appreciable quantity of ammonia. I have not examined this change in detail, but it is obvious that one of the direct products of the reaction is sulphocyanate of ammonium, the further decomposition of which explains the appearance of the disulphide of carbon as well as the other products observed. The residue, of course, must contain the varied compounds generated by the action of heat on sulphocyanate of ammonium.

Behaviour of the Arsines and Stibines with the Sulphocyanates of Phenyl and Allyl.—The facility with which the compound ureas containing nitrogen and phosphorus are formed, induced me to attempt the production of analogous compounds with arsenic or antimony in place of phosphorus. I therefore treated sulphocyanate of phenyl and oil of mustard successively with triethylarsine and triethylstibine, first at ordinary and then at gradually increasing temperatures in sealed tubes. But not one of these experiments led to the expected result. The arsines and stibines differ, indeed, in their chemical character, much more from ammonia than the phosphines. Their incapability of forming saline compounds with acids is alone sufficient to render the formation of ureas containing arsenic and antimony somewhat improbable. When mixtures of triethylarsine with sulphocyanate of phenyl on the one hand, and sulphocyanate of allyl on the other, were left to stand for some time at ordinary temperatures, the liquid in both cases was found to be traversed by a small quantity of beautiful needle-shaped crystals. The crystals from both mixtures were found to be the same; they were readily identified with the beautiful needles

which are gradually formed in triethylarsine when left in contact with atmospheric air.

Behaviour of Triethylphosphine with Cyanates.—The formation of sulphuretted ureas containing phosphorus and nitrogen led me to try whether the corresponding oxygen-compounds could likewise be produced.

When *cyanate of phenyl* is mixed with the phosphorus-base, great heat is evolved, indicating a marked chemical reaction. The mixture on cooling solidifies into a mass of shining crystals which are insoluble in water, nearly insoluble in ether, and dissolve with difficulty even in boiling alcohol. By recrystallization from the last-mentioned solvent, the new body is easily obtained pure. The further examination of the resulting crystals proved, however, that they by no means consisted of the compound urea of which I was in search. From the analysis, which I intend to give in connexion with other researches, it appeared that the crystals still possessed the composition of cyanate of phenyl, that, indeed, they were *cyanurate of phenyl*. The triethylphosphine in this case appears to induce nothing more than a new molecular disposition of the elements in cyanate of phenyl. The peculiar character of this metamorphosis may be perceived in the most beautiful manner by dipping a glass rod moistened with triethylphosphine into a considerable quantity of cyanate of phenyl. The liquid immediately becomes hot, and solidifies after a few seconds into a shining crystalline mass of the cyanurate.

Similar results were obtained by the action of the phosphorus-base on *cyanate of ethyl*. The two bodies may be mixed without evolution of heat, and the mixture does not solidify; but the transformation is soon indicated by the diminution of the penetrating odour of the cyanate. If, as soon as the odour has disappeared, the liquid be mixed with dilute hydrochloric acid, which removes the free phosphorus-base, the oil which floats on the surface quickly solidifies into a solid crystalline mass which, when recrystallized from boiling water, exhibits all the properties of *cyanurate of ethyl*.—When a stream of *cyanic acid* gas is passed through triethylphosphine, the odour of the acid disappears, while the phosphorus-base becomes turbid, and yields a white deposit of *cyanuric acid*.

In connexion with these experiments, I have had occasion to

convince myself that *cyanic acid* gas and *phosphoretted hydrogen* do not act upon one another, at least at ordinary temperatures.—I was anxious to ascertain whether the peculiar action of the phosphorus-base on the cyanates extended likewise to the cyanides. I found, however, that *cyanide of methyl* (acetonitrile) or *cyanide of phenyl* (benzonitrile) may be left for days in contact with the phosphorus-base at temperatures varying from 100° to 150°, without experiencing the slightest alteration. Had these substances been changed under the above conditions, like the cyanates, their transformation into methyl- and phenyl-compounds corresponding to cyanethine might have been expected.

Experiments in the Methyl-series.—The information which I have collected with reference to the phosphorus-compounds, has been almost exclusively obtained by the study of triethylphosphine. In exceptional cases only have I worked in the methyl-series. Trimethylphosphine, on account of its volatility, is much less easily prepared than the ethyl-compound, and especially much more difficult to preserve. This body is oxidized with such rapidity, that it disappears from the hand of the operator during manipulation. Its odour, moreover, is insupportable for any length of time.

Nevertheless, I have made a few experiments with the methyl-compound, a slight sketch of which may form the conclusion of this paper.

The phosphorus-derivatives of the methyl-series exhibit the most perfect analogy with the corresponding ethyl-compounds.

Oxide of trimethylphosphine produces with iodide of zinc, with dichloride of platinum, and with trichloride of gold, the homologues of the several compounds obtained from the oxide of triethylphosphine.

When trimethylphosphine, either pure or dissolved in alcohol and ether, is submitted to the action of disulphide of carbon, all the phenomena are reproduced which I have mentioned at some length in describing the corresponding ethyl-base. The red crystals which are formed are somewhat paler, much more volatile, and much more readily altered. The disulphide-of-carbon-compounds of the methyl- and ethyl-series exhibit in their properties the same relation which obtains between the sulphides of the two series.

Y 2

The formula

$$C_4H_9PS_2 = (CH_3)_3P, CS_2$$

was established by analysis.

The red crystals are changed with the utmost facility into sulphide of trimethylphosphine. In the hope of forming fine crystals, similar to those obtained with the ethyl-compound, a solution of the red crystals in warm ether was allowed to cool in a tall open cylinder. When the solution was examined next morning, it had become colourless, leaving, upon spontaneous evaporation, the beautiful crystals of the sulphur-compound.

The sulphocyanates of phenyl and allyl readily combine with trimethylphosphine. The reaction is even more powerful than with the ethyl-base. The urea-body, which trimethylphosphine produces with sulphocyanate of phenyl, is a liquid which I have not been able to obtain in the solid state. Directly prepared from the constituents, or separated from one of its crystalline salts, it forms a slightly coloured oily liquid, soluble in water, difficultly soluble in ether, readily soluble in alcohol. On adding concentrated hydrochloric acid to the oil, it gradually solidifies to a crystalline mass of sulphur-yellow delicate, hair-like needles, which may be recrystallized both from water and from alcohol. I have fixed the composition of this phosphoretted urea by a chlorine-determination in a chloride of the composition,

$$C_{10}H_{15}NPSCl = \left[\left. \begin{matrix} (CS)'' \\ H(CH_3)_2 \\ (CH_3)(C_6H_5) \end{matrix} \right\} NP \right] Cl.$$

The brown liquid which is formed, with considerable evolution of heat, when trimethylphosphine is brought in contact with mustard oil, gradually deposits well-formed transparent colourless prisms, the habitus of which resembles that of the corresponding ethyl-compound. The crystals were not analysed, but there can be no doubt that they were the methylated phosphorus-urea of the allyl-series:

$$C_7H_{14}NP = \left. \begin{matrix} (CS)'' \\ (CH_3)_2 \\ (CH_3)(C_3H_5) \end{matrix} \right\} NP.$$

Phosphoretted hydrogen is without action on the sulphocyanates of phenyl and allyl.

In conclusion, I beg to thank Drs. A. Leibius and M. Holzmann for their assistance in some of the experiments connected with this inquiry.

XXVI.—*On the Discrepancies in the Statements of Pelouze and F. Mohr, respecting the Solubility of Gallotannic Acid in Ether.*

By Professor Bolley.

For the extraction of tannic acid from coarse gall-nut powder, in his "Displacement Apparatus," Pelouze recommends the use of ordinary, not absolute, ether. The liquid which then runs off, separates into two layers, the lower of which is thickish, while the upper is mobile and less coloured. The lower liquid contains the tannic acid, and is regarded by Pelouze as a solution of tannic acid in water; the upper liquid is stated to be ether, holding in solution small quantities of tannic acid, colouring matter, &c.

Mohr, in his commentary on the Prussian Pharmacopœia, decidedly contradicts this statement. His view of the matter has found its way into most Manuals of Chemistry, articles in Chemical Dictionaries, &c., and is generally received as correct. He regards the lower stratum of liquid above-mentioned as *a concentrated solution of tannic acid in ether*, and the upper, as *ether* which has dissolved only a small quantity of tannic acid. The two layers, he maintains, are not soluble one in the other. If this be so, it affords another example of a condition hitherto known to exist in one instance only (that of coniine), in which the solution of a body in a certain solvent is not diluted by contact with that same solvent. In spite of this anomaly, Mohr's statement has been adopted without experimental verification. Mohr rests his view on an experiment described by himself. On treating tannic acid with anhydrous ether, he obtained the thickish layer already men-

tioned, and above it there floated a stratum of ether, containing only a small quantity of tannic acid.

I have likewise examined this peculiar phenomenon. I find that *anhydrous ether* (previously decanted several times over chloride of calcium, boiling at 34·9° C., and having a specific gravity of 0·724 at 11·25° C.), takes up but a very small quantity of tannic acid, indeed scarcely any (0·206 p. c. at 5° C.), while the greater part of the tannic acid remains in the liquid in the form of a dry compact powder. On mixing the ether with half its volume per cent. of water, the thickish liquid is formed. The ether—the upper layer—when mixed with a little water, takes up rather more tannic acid than the anhydrous ether. I find that the upper layer—pure ether with 1 vol. p. c. of water—takes up 1.2 p. c. tannic acid.

This result appears to confirm Pelouze's view. It is not however true that the syrupy layer is a concentrated aqueous solution of tannic acid. On carefully removing a portion of this liquid, so that none of the upper stratum may mix with it, introducing it into a retort, and distilling with good condensation, considerable frothing takes place at first, and ether passes over, followed by water, the two liquids forming layers of equal depth in a cylindrical receiver.

If a little water be added to these two liquids, a third layer is formed, which rests between the two, and is therefore insoluble both in ether and in water. This behaviour appears to me to render probable the existence of a chemical compound of tannic acid, ether, and water, possibly an acid ethyl-salt constituted like ethyl-sulphuric acid, that is to say, a *tannate of ether and water*.

There is a practical deduction from these experiments which deserves to be mentioned. The behaviour of pulverized and well dried tannic acid to ether, is so peculiar that it may be used as a test of the presence of water in that liquid. In anhydrous ether the powder remains quite unaltered, but in hydrated ether it cakes together or deliquesces to a thickish syrup, according to the amount of water present, and the quantity of tannic acid added. Very small quantities of tannic acid give a distant reaction.

XXVII.—*On the Colouring Matters of Persian Berries, and on certain general relations of Yellow Vegetable Dyes.*

By Professor Bolley.

The chemical investigations hitherto published respecting Persian Berries (*Yellow berries, graines d'Avignon, Krautzbeeren*) may be epitomized as follows :—

Kane* distinguishes two colouring matters : (a). *Chrysorhamnin*, a yellow substance which may be extracted by ether, crystallizes in needles, is nearly insoluble in cold water, but easily soluble in ether. It contains, according to the mean of two analyses, 58·02 per cent. of carbon and 4·70 p. c. hydrogen, and is said to be decomposed by solution in hot alcohol or water and boiling of the solution, yielding another colouring matter (b), called *Xanthorhamnin*, which is soluble in water and alcohol, but insoluble in ether, and when dried at 320° F. contains 52·55 C. and 5·15 H.

Gellatly† obtained, with ether, neither chrysorhamnin nor any other characteristic substance, but with alcohol he obtained a yellow substance, crystallizing in needles, easily soluble in water, whether cold or hot, insoluble in ether and containing (when dried at 100° C.) 52·10 % C. and 5·78 H. This body he regarded as xanthorhamnin in a tolerably pure state. It is decomposed by heating with dilute sulphuric acid, yielding, together with glucose, a body called *Rhamnetin*, soluble in water, alcohol, and ether, and containing 59·41 % C. and 4·38 H.

Hlasiwetz,‡ in his paper on quercitrin, makes some observations on Gellatly's experiments, chiefly, however, with reference to the elementary analyses. The nature of his suggestions may be understood from the following table :—

Percentage of carbon and hydrogen in

Quercitrin at 100° according to Bolley (1841) according to Hlasiwetz (1859)	Kane's Xanthorhamnin.	Gellatly's Xanthorhamnin.
C = 52·49	52.55	52·10
H = 5·03	5·15	5·78
Rigaud's Quercetin.	**Chrysorhamnin.**	**Gellatly's Rhamnetin.**
C = 59·23	58·02	59·41
H = 4·13	4·70	4·38

* Phil. Mag., July, 1843, p. 3. † Edinb. New Phil. Jour. vii, 252.
‡ Ann. Ch. Pharm. cxii, 96.

Hlasiwetz regards xanthorhamnin as identical with quercitrin, and rhamnetin as identical with quercetin, but he has not made any original researches on Persian berries.

With the view of clearing up some of the above-mentioned discrepancies, I have likewise made an investigation of Persian berries. In the first place I must observe that I obtained an abundant extract with *crude ether* (this may perhaps explain the differences between the statements of Kane and Gellatly). This extract, after the ether had been evaporated, the residue taken up by alcohol, the solution filtered, and the alcohol evaporated, with addition of water,—yielded stellate groups of yellow needles, which were not altered by repeated solution, boiling and precipitation.

I analysed two different portions of this substance, and obtained from the one

$$C = 58{\cdot}87 \text{ per cent.}$$
$$H = 4{\cdot}66 \quad ,,$$

and from the other which was dried for a longer time at about 120° C.

$$C = 60{\cdot}239 \text{ per cent.}$$
$$H = 4{\cdot}180 \quad ,,$$

These crystals are somewhat soluble in pure ether, sparingly in water, easily in alcohol. Their solution gives with *neutral acetate of lead*, a brick-red precipitate; with *nitrate of silver*, a blood-red liquid, and afterwards reduced silver. I found some time ago that the lead precipitate is peculiarly characteristic of quercetin, and I have now to make a similar observation respecting the silver reaction: quercetin behaves both with lead and with silver solutions precisely in the manner just described. The crystallized colouring matter which I obtained by the above process is beyond all question identical with quercetin. The peculiar interest of this fact is that it demonstrates the *pre-existence in a vegetable substance of a product of the decomposition of quercitrin.*

Chrysorhamnin (which Gellatly did not obtain) is perhaps the same as quercetin; but, from the preceding observations, it appears doubtful whether this body can easily decompose and yield a substance like that which Kane describes under the name of xanthorhamnin. If therefore, as Hlasiwetz supposes, rhamnetin is identical with quercetin, it follows that

decomposition is not necessary to the production of rhamnetin. Or may it not be possible that this decomposition takes place spontaneously in some kind of yellow berries? Several varieties of these berries are in fact distinguished according to their appearance and their origin. This assumption, which is by no means improbable, may perhaps serve to reconcile some of the contradictions in the statements of Kane and Gellatly.

XXVIII.—*On a hitherto unobserved source of Paraffin.*

By Professor Bolley.

Masses of naturally separated paraffin have been found in deposits of rock-oil, *e. g.*, at Borystow in Gallicia; and Ozokerite, Scheererite, Idrialin, &c., afford proof that hydrocarbons differing considerably in melting point and chemical composition occur ready formed in nature; but paraffin, which occurs in tar and in certain mineral substances used for the production of heat and light, has hitherto been regarded as a product of the action of heat.

In the Technical Laboratory of the Swiss Polytechnic School, researches are at present being made on certain kinds of coal used for the production of illuminating gas; and one result of these researches, easily detached from the rest, I am now about to communicate.

Boghead shale—which, according to Gœppert, is not a true coal—has been examined by several chemists, with reference to the quantity and composition of the residue which it leaves when heated, and the nature of the volatile products. I have endeavoured to ascertain the nature of some of its proximate constituents by exhausting them with various reagents. A kilogramme of pulverized Boghead cannel coal yielded to alcohol 2·14 parts of solid extract residue; and to ether, after drying, 2·63 pts. The alcoholic extract presented less interest than that obtained with ether, which was unctuous to the touch and not very deeply coloured. I found that it could be redissolved in ether, and decolorised by agitation with animal charcoal. After this treatment, however, the residue exhibited by elementary analysis a quantity of oxygen amounting to 11 per cent., and gradually turned yellowish when

heated for some time in the water-bath above its melting point. It sustained a slight loss by boiling with soda-lye, and the undissolved portion melted at 41° C, remained colourless when heated, solidified in crystalline laminæ, was insoluble in water, sparingly soluble in alcohol, somewhat more soluble in ether. The analysis of this residue gave

Carbon	86·33	per cent.
Hydrogen	13·32	„
	99·65	

The melting point of paraffin was found by Reichenbach to be 43° C. We know, however, that different samples of paraffin, both natural and artificial, melt, some at higher, some at lower points, so that this circumstance need not prevent us from regarding the substance in question as paraffin.

To me it appears probable that paraffin exists, as such, in several of the materials from the distillation-products of which it has hitherto been prepared, such as peat, shale, lignite, &c., and the process of separation just described affords a convenient method of testing such substances with reference to their utility for the preparation of paraffin, which has hitherto been done exclusively by dry distillation.

I must further remark, that from two sorts of coal which I examined in this way, I obtained, not paraffin, but extracts more of the nature of asphalt. It is commonly stated that the non-existence or the rarity of occurrence of paraffin in coal-tar is attributed to the great heat employed in the distillation. May it not rather be due to the fact that true coal does not contain paraffin ready formed, and therefore cannot yield a tar containing paraffin?

XXIX.—*Note of the Action of Chloride of Ethyl upon Ammonia.*

By Charles Edward Groves.

It has often struck me as remarkable, that while the deportment of ammonia with the bromide and iodide of ethyl had been so carefully studied, the action of this substance upon the chloride of ethyl should scarcely have been noticed. Although the difficulty of manipulating so volatile a substance as chloride of ethyl promised but little advantage in the practical preparation of the ethyl bases; it appeared nevertheless desirable to examine the reaction, in order to complete the history of the formation of these substances. When chloride of ethyl sealed up in stout glass tubes with about three times its bulk of alcoholic ammonia — formed by nearly saturating alcohol with dry ammonia — was digested for six or seven hours at the temperature of 100° C., a large quantity of a white crystalline substance was deposited in the tubes, apparently consisting of chloride of ammonium. The tubes were then opened and the contents thrown on a filter, the white crystalline powder washed with absolute alcohol, and the filtrate evaporated to dryness on the water-bath, to expel alcohol and excess of ammonia. The residue was then dissolved in water, filtered, and submitted in a retort to the action of an excess of oxide of silver, in order to set free the bases formed during the reaction. On heating the mixture, the whole of the volatile bases passed over. The residue in the retort, consisting of oxide and chloride of silver, together with the hydrated oxide of a non-volatile ammonium-base, was thrown on a filter and washed with water until the washings were no longer alkaline. The filtrate neutralized with hydrochloric acid, evaporated to a small bulk on the water-bath, and filtered, yields with bichloride of platinum, a yellow crystalline precipitate, which was washed with a small quantity of cold water and recrystallized from boiling water.

0·185 grammes of substance yielded 0·0545 grammes of platinum; this shows a percentage of platinum equivalent to 29·4 per cent. The formula—

$$(C_4H_5)_4NClPtCl_2$$

requires 29·44 per cent. of platinum. The non-volatile base produced in the reaction between chloride of ethyl and ammonia, is

therefore, as might have been expected, the hydrated oxide of tetrethylammonium. The alkaline distillate, containing the volatile portion of the bases was neutralized with hydrochloric acid, evaporated to a small bulk on the water-bath, and precipitated with an insufficient quantity of bichloride of platinum. The precipitate, consisting of thin crystalline hexagonal plates, was recrystallized from a small quantity of water, to which it was found convenient to add a few drops of alcohol, the salt being rather insoluble in dilute alcohol.

0·235 grammes of substance gave 0·092 of platinum.

The formula—

$$[(C_4H_5)\ H_3N]\ Cl,\ Pt\ Cl_2$$

requires 39·29 per cent. of platinum and the analysis gave 39.15 per cent.

This result shows the existence of ethylamine among the volatile products of the action of chloride of ethyl upon ammonia.

By successive partial precipitations and recrystallizations, a considerable quantity more of the platinum-salt of ethylamine was separated; until at last a very small quantity of another and more soluble salt was deposited from the mother-liquors. After a single recrystallization, which was all that was possible, owing to the amount being so small, it was dried and analysed; and although some crystals of the ethylamine platinum-salt could be discerned by the microscope, it gave results which approximated closely with the theoretical percentage of the diethylamine platinum-salt.

0·170 of substance gave 0·062 of platinum;

this gives a percentage of 36·47 of platinum.

The formula—

$$[(C_4H_5)_2H_2\ N]\ Cl,\ PtCl_2$$

requires 35·35 per cent of platinum. The above platinum determination might also represent a mixture of the salt of ethylamine and triethylamine; but the compound analysed, although more soluble in water than the ethylamine-salt, was not nearly so soluble as the salt of triethylamine; moreover the latter substance is easily recognised by its crystalline form. In addition to the salts above mentioned, a small quantity of triethylamine was, in all probability, present among the products of the reaction of

chloride of ethyl upon ammonia; but owing to the small proportion in which it existed, and the known solubility of its platinum-compound, I have not been able to establish its formation by experiment.

The following equations represent the action of chloride of ethyl upon ammonia:—

$$H_3N + C_4H_5Cl = [(C_4H_5), H_3N]\ Cl$$
$$2\,H_3N + 2C_4H_5Cl = [(C_4H_5)_2H_2N]\ Cl + H_4NCl$$
$$4\,H_3N + 4C_5H_5Cl = [(C_4H_5)_4\ \ N]\ Cl + 3H_4NCl.$$

The experiments which I have described show a marked difference in the action of the chloride when compared with that of the bromide and iodide of ethyl. The chloride of ethyl produces almost exclusively the chloride of ethylammonium, together with small quantities of the chlorides of diethylammonium and tetrethyl-ammonium. The bromide of ethyl, according to the experiments of Dr. Hofmann, gives chiefly the bromide of ethylammonium, but also very appreciable quantities of the bromides of diethyl- and triethylammonium, with but a small proportion of the tetrethyl-ammonium-compound; and lastly, the iodide produces the three volatile bases in about equal proportions, but generally very appreciable quantities of the tetrethyl-ammonium-compound.

The above experiments were performed in the Laboratory of Dr. Hofmann.

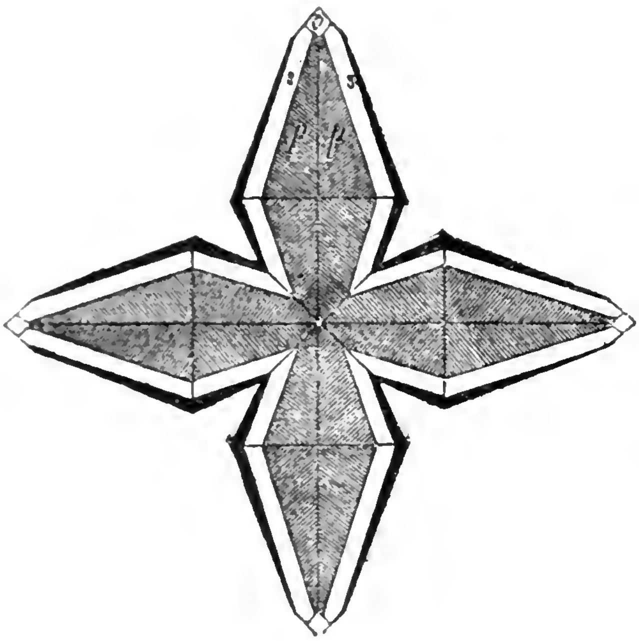
XXX.—*On the Crystalline Form of Metallic Chromium.*

By Professor Bolley.

The preparation of sesquichloride of chromium and of crystallized metallic chromium by the methods recently given by Wohler,* is very easy. I entrusted the preparation to one of the students in my laboratory, who obtained a product exhibiting the colour and lustre of the crystalline powder described by Wöhler. Wöhler says of this substance—"It exhibits, even with a magnifying power

* Leichte Darstellungsweise des metallischen Chroms. (Ann. Ch. Pharm. cxi, 230.)

of 50, crystalline aggregations having the form of fir-branches interspersed with very beautiful *Rhombohedrons* of great lustre and nearly tin-white colour." I have examined the crystalline mass with a magnifying power of 85, and have found that it contains numerous fir-shaped arborescences such as Wöhler describes. But it was immediately apparent that the loose crystals dispersed through the mass were referable, not to rhombohedral but to octohedral primary forms. These crystals are *very frequently* united in groups of four, in the shape of a cross, but the smallness of the crystals precluded the possibility of measurement. My colleague, Professor Kenngott, has had the goodness to determine the form of these crystals, and finds that they are octohedrons belonging to the quadratic system. They are for the most part octagonal pyramids *p, p,* combined with a more acute pyramid *s,* and a more obtuse pyramid *o.* The *p*-faces are very deeply striated; the *o*-faces very smooth and shining.



It is well known that the crystalline forms of the metals belong chiefly to two systems, the ductile metals crystallizing in the tesseral, the brittle metals in the rhombohedral system, while some are dimorphous, and exhibit forms belonging to both these systems. Hitherto *tin* is the only metal known to crystallize in another system, viz., the quadratic. *Boron* likewise, according to Quintino Sella,* crystallizes in the quadratic system.

Chromium affords, therefore, the third example of an elementary body, differing from most others in its crystalline form. It follows also from these observations, that although certain compounds of chromium are isomorphous with the analogous compounds of iron, this isomorphism does not exist in the metals themselves.

* Sulle forme cristalline di alcuni sali di platino e del Boro adamantino, par Quintino Sella. Torino, 1857.

XXXI.—*On a new Lead-salt, corresponding to Cobalt-yellow.*

By S. D. Hayes, Edinburgh University.

In the course of some investigations on the cobalto-cyanide compounds, I was obliged to use a quantity of cobalt-yellow, the pigment discovered by M. Saint Evre, in 1852.* All the methods described for preparing this salt are very tedious, so that it became an object to find a more ready means. The best method hitherto given, is to precipitate a solution of nitrate of cobalt with an excess of potash; then by passing a current of deutoxide of nitrogen (NO_2) through the mass, the cobalt-yellow is obtained: but the greater part of the deutoxide passes through without being absorbed; the experiment requires hours; and the amount of salt obtained is very small.

As the composition of this body is considered doubtful, it occurred to me that it might be made from peroxide of nitrogen (NO_4), and after a few trials I obtained it very readily, in large quantities, and found that all the cobalt contained in a solution may thus be converted into cobalt-yellow. Two bottles, connected and supplied with funnel tubes, are about half filled with a solution of nitrate of cobalt, to which potash, slightly in excess, is added. On passing a brisk current of peroxide of nitrogen through the liquid, the mass in the first bottle soon changes colour, and the pigment begins to fall; by adding small quantities of potash, occasionally, through the funnel-tubes, all the cobalt may be removed. The peroxide of nitrogen is most readily prepared by allowing a current of the deutoxide, produced from copper and nitric acid, in a small flask, to mix with a current of common air from a gasometer, in a dry empty bottle, before passing into the cobalt-solutions. The current of air can be regulated at the gasometer, and the flask for generating the deutoxide can be easily removed and replenished when necessary. A solution of the carbonate may be used instead of caustic potash, for precipitating the cobalt-solutions, with the same results.

A. Stromeyer, when working upon this salt, endeavoured to obtain an analogous body with lead; he succeeded in getting a

* Ann. Ch. Phys., [3],xxxviii, 177.

yellow solution by means of nitrite of potash and acetic acid, in a solution of lead, but he then added cobalt which gave a precipitate.*

On treating a solution of nitrate of lead with potash, and passing a current of peroxide of nitrogen through the liquid, precisely as in making the cobalt-yellow, I found that all the peroxide was absorbed, and as the oxide of lead disappeared, the solution became very yellow. Evaporating and crystallizing this, I obtained large yellow prismatic crystals; nitrate of potash crystallizes at the same time, and if the peroxide of nitrogen has been passed through the lead too long, nitrate of lead is formed.

The yellow salt was easily separated and recrystallized. The bases were determined as sulphates, in the analyses, with the following results:—

I. 0·7462 grms. pure salt gave 0·4200 grms. sulphate of lead and 0·0097 grms. lead = 0·319493 grms. oxide of lead, and 0·2472 grms. sulphate of potash = 0·133545 grms. potash.

II. 1·4590 grms. gave 0·6387 grms. oxide of lead and 0·25931 grms. potash.

III. 1·0271 grms. gave 0·43745 grms. oxide of lead and 0·1881 grms. potash.

The nitrogen was determined as gas, metallic copper reduced from the *fine* oxide, being used in the combustion tube with a little oxide at the fore end. The gas was collected and washed in a small apparatus, then transferred to the eudiometer, where it was measured.

I. 0·1926 grms. salt, gave 45·6277 cubic centimeters nitrogen at temperature 6·0°C.; and pressure 277·5 millimeters = 16·30 cc., at 0°C. and 760 mil. pressure, = 0·204822 grms.

II. 0·1958 grms. gave 16·23 cc. at 0°C. and 760 mil. pressure, = 0·225983 grms.

The water was determined by combustion with metallic copper.

I. 0·7834 grms. gave 0·0274 grms. water.

II. 0·9145 grms. gave 0·0314 grms. water.

III. 0·4735 grms. gave 0·0177 grms. water.

* Ann. Ch. und Pharm., xcvi, 228.

	I.	II.	III.	IV.
Oxide of lead . . .	42·81	43·08	42·59	43·22
Potash	17·90	17·77	18·31	,,
Nitrogen	10·63	,,	10·35	,,
Water	3·47	3·43	3·73	,,
Oxygen by difference	25·16	,,	25·02	,,
	100·00		100·00	

The above analyses correspond to the following calculated formula :—

PbO . . .	111·56	42·98
KO . . .	47·00	18·10
N_2	28·00	10·78
O_8	64·00	24·67
HO . . .	9·00	3·47
	259·56	100·00

As this salt crystallizes out with nitrate of potash, it is of about the same degree of solubility, in either hot or cold water, and the solution may be boiled for some time without any decomposition, but it is readily decomposed by sulphuric, hydrochloric, or nitric acid, giving off red fumes. With the common reagents, it acts like nitrate of lead, but with a solution of sulphate of cobalt, it gives cobalt-yellow, which goes down with the sulphate of lead. It loses its atom of water at 100°C., but if the temperature be raised a few degrees higher, the red fumes come off abundantly. The crystals are of a bright yellow colour, and remain unaltered in the air.

I am not yet prepared to give my salt any decided *rational* formula, but its composition may be expressed in several ways as below. When $2NO_4$ is passed over 2KO, we get $KONO_5$ and $KONO_3$, two distinct salts; but if $2NO_4$, be passed over CoO and KO, as in the case of cobalt-yellow, or over PbO and KO, as in this salt, we get only one salt of a double composition, which we may write in like manner:

$$KONO_3, CoONO_5, \text{ or}$$
$$KONO_3, PbONO_5 + HO.$$

But there is an objection to this, as cobalt-yellow is almost

insoluble in water. These salts may also be looked upon as double peroxides, in which two equivalents of oxygen have been replaced by two equivalents of NO_4, thus

$$\left\{\begin{matrix} PbO, NO_4 \\ KO, NO_4 \end{matrix}\right\} + HO;$$

but from the nature of the salts I hardly think that NO_4 exists in them. However Gmelin describes a salt to which he gives the formula $2PbO, NO_4$, aq.,* and we express the composition of these salts, just as well, by writing them thus,

$$KONO_4, CoONO_4; \text{ or}$$
$$KONO_4, PbONO_4 + HO.$$

This subject will be pursued, and I hope to get several other salts, which must give some reactions that will lead to the right rational formula.

These experiments were made in the laboratory of the Edinburgh University.

XXXII.—*On the Electrolytic Test for Arsenic, and on the Presence of that Metal in certain Reagents.*

By Charles L. Bloxam.

In a former communication upon this subject which I had the honour of presenting to the Society,† it was shown that when a solution containing arsenious acid is mixed with diluted sulphuric acid and subjected to the action of the voltaic current, arseniuretted hydrogen is evolved at the negative terminal, and that in this way very minute quantities of arsenious acid can be detected with great certainty, even in the presence of large quantities of organic matter, and without adding any material to the liquid which would interfere with its examination by other analytical processes. It was also stated that arsenic acid did not respond to this test, and that the presence of mercury in the liquid interfered very materially with the detection of the arsenic.

* Handbuch. Bd. 3, s. 142.
† See page 12 of this volume.

It is the object of this paper to show how arsenic acid may be brought within reach of this test, how the interference of mercury may be prevented, and how all chance of error due to the evolution of antimoniuretted hydrogen may be avoided.

The form of apparatus recommended in the previous notice admitted of some obvious improvements. A tube-funnel has been added, to permit the introduction of the liquid to be tested, and the platinum wires communicating with the battery have been replaced by broad strips of platinum foil.

If arsenious acid be converted into arsenic acid by boiling with hydrochloric acid and chlorate of potassa, and the solution be poured into the diluted sulphuric acid during the passage of the current, no arseniuretted hydrogen is evolved; but if a few drops of solution of sulphurous acid or of bisulphite of soda be poured down the funnel-tube, a greenish yellow iridescent crust of tersulphide of arsenic is almost immediately deposited at a little distance beyond the heated portion of the tube, and is followed, in most cases, by the usual mirror of metallic arsenic.

Since arsenic acid is reduced with great difficulty by sulphurous acid at the ordinary temperature, it appeared probable that the effect was really due to the hydrosulphuric acid formed by the action of the nascent hydrogen upon the sulphurous acid, and accordingly it was found that the introduction of a few drops of solution of hydrosulphuric acid into the electrolytic cell also caused the evolution of arseniuretted hydrogen.

If an excess of hydrosulphuric acid be employed, a deposit of sulphur is formed in the tube, nearer to the orifice than the deposit of sulphide of arsenic, from which it may be very easily distinguished by its much lighter colour, and by its insolubility in a warm solution of sesquicarbonate of ammonia, which readily dissolves the sulphide of arsenic.

Three experiments may be especially referred to in evidence of the certainty attending this process.

0·01 grn. of arsenious acid was boiled with hydrochloric acid and chlorate of potassa, and introduced into the electrolytic apparatus, and the reduction-tube through which the hydrogen escaped was heated to redness for 30 minutes without any appearance of deposit; but, on adding 5 grn. measures of a solution of bisulphite of soda, a yellow crust of tersulphide of arsenic made its appearance in 5 minutes, and was followed by a distinct deposit of

metallic arsenic, identified by its volatility and its solubility in chloride of lime.

In a second similar experiment, 10 grn. measures of a saturated solution of hydrosulphuric acid were poured down the funnel-tube, instead of the bisulphite of soda. The crust of sulphide appeared within 10 minutes, and that of metallic arsenic within 15 minutes.

A third experiment was made with only 0·001 grn. of arsenious acid which had been boiled with hydrochloric acid and chlorate of potassa; within 13 minutes after the addition of 10 grn. measures of hydrosulphuric acid, the yellow sulphide of arsenic appeared in the tube.

It was found that however large a proportion of hydrosulphuric acid was poured into the decomposing cell, the arsenic was still evolved, the metal combining with the nascent hydrogen in preference to the sulphur. It appeared probable, however, that the addition of hydrosulphuric acid would at once precipitate any antimony or mercury present in the liquid under examination, and would prevent their interference with the detection of the arsenic.

One grain of tartar-emetic (0·36 grn. Sb) dissolved in water, was slightly acidulated with sulphuric acid, mixed with an excess of hydrosulphuric acid, and poured, without filtering, into the decomposing cell in which the diluted sulphuric acid was undergoing electrolysis; the evolution-tube was maintained at a red heat for 38 minutes without any deposit in the tube except a thin film of white sulphur.

Another grain of tartar-emetic was then mixed with 0·01 grn. of arsenious acid, which had been boiled with hydrochloric acid and chlorate of potassa, and the mixture was treated with an excess of hydrosulphuric acid, and poured into the same decomposing cell without interrupting the experiment. In 5 minutes, yellow rings of tersulphide of arsenic made their appearance in the capillary reduction-tube; in less than 15 minutes, a distinct crust had formed, presenting exactly the same appearance as if no antimony whatever had been present. No deposit had been formed upon the negative plate.

In the next trial, only 0·001 grn. of arsenious acid was mixed with 1 grn. of tartar-emetic; the solution was boiled with hydrochloric acid and chlorate of potassa, diluted to one fluid ounce with

water, saturated with hydrosulphuric acid gas, and poured, with the suspended precipitate, into the decomposing cell. Within 15 minutes, a distinct deposit of metallic arsenic was obtained, which dissolved immediately in solution of chloride of lime.

When 1 grn. of tartar-emetic and 0·01 grn. of arsenious acid were mixed with considerable quantities of bread, milk, and beer, and the brown treacly liquid obtained by boiling with hydrochloric acid and chlorate of potassa, and subsequent evaporation, was mixed with excess of hydrosulphuric acid and poured into the decomposing cell, deposits of metallic arsenic and of the tersulphide were almost immediately formed in the tube. On collecting the dark precipitate after the operation, it was easily identified as sulphide of antimony.

In a second experiment of this description, one-fourth of the brown fluid (containing 0·09 grn. Sb and 0·0025 grn. AsO_3) was introduced into the decomposing cell without adding hydrosulphuric acid, when a very distinct mirror of antimony was, of course, formed in the reduction-tube, and a deposit of that metal was obtained on the negative plate. The reduction-tube was then changed, and hydrosulphuric acid added, when deposits of arsenic and its sulphide, free from antimony, were formed in the tube.

To prove that with this modification of the test, the presence of mercury no longer prevented the detection of arsenic, experiments precisely similar to those above described were made, respectively, upon mixtures of 1 grn. corrosive sublimate with 0·01 grn. arsenious acid, and 0·25 grn. corrosive sublimate with 0·0025 grn. arsenious acid, mixed with white of egg, bread, milk, and beer, when no difficulty whatever was found in the detection of the arsenic.

The solution containing chloride of mercury and arsenic acid was electrolytised for half an hour without the slightest appearance of arsenical deposit in the heated tube, the mercury being deposited abundantly upon the negative plate; but on the addition of solution of hydrosulphuric acid, a crust of metallic arsenic was soon obtained.*

* It will be evident that this method of converting the arsenic into arsenic acid and precipitating the antimony and other metals by hydrosulphuric acid, in the *cold,* may be employed with advantage in Marsh's test; the solution containing the arsenic acid must be filtered, however, before introduction into the evolution bottle, as the suspended sulphide of antimony was found to be immediately decomposed in

In order to ascertain whether the occurrence of putrefaction in an organic mixture containing arsenious acid would interfere with its detection by the electrolytic test, an experiment was made with 0·001 grn. of arsenious acid mixed with meat, white of egg, beer, bread, and milk, and allowed to putrefy for nearly twelve months. No difficulty was experienced in detecting the arsenic.

I am very desirous of convincing myself that reliance may, in all cases, be placed on this process for the detection of arsenic, by operating upon organic matters *exactly similar* in their nature and quantity to those often submitted to the chemist in judicial inquiries, but have hitherto been unable to do this, in consequence of the difficulty of procuring hydrochloric acid so pure that, when examined in the large quantity required for the disintegration of considerable masses of viscera, it did not afford any indication of the presence of arsenic. Believing that I possessed a quantity of sulphuric acid perfectly free from arsenic, I employed it for the preparation of hydrochloric acid; but even this sample was not found to be absolutely free from the impurity, and on resorting to the sulphuric acid, the examination of a large quantity at once proved the presence of a very minute proportion of arsenic, which was more easily traced in the hydrochloric acid, since the latter could be employed without inconvenience in larger quantity, both in the electrolytic and in Marsh's test. The production of sulphuric acid absolutely free from arsenic is now engaging my attention.

It has also been incidentally noticed in the course of these experiments, that various samples of solution of potassa and of the solid hydrate contained very notable quantities of arsenic, attributable probably to their having been prepared from nitre by the action of (arsenical) copper at a high temperature.

A more important point for the consideration of the analytical chemist is the occurrence of arsenic in the hydrosulphuric acid,

contact with zinc and sulphuric acid. In a mixture containing a grain of tartar-emetic and one-hundredth of a grain of arsenious acid, the latter was detected as easily as if no antimony had been present, by boiling with hydrochloric acid and chlorate of potassa, precipitating the cold solution with excess of hydrosulphuric acid, filtering, and pouring into Marsh's apparatus.

In Marsh's test, the use of electrolytised zinc was found to be attended with advantage in minute investigation, on account of the very slow and steady evolution of gas.

prepared in the usual manner from sulphide of iron and diluted sulphuric acid. On passing the gas for 10 or 15 minutes through a reduction-tube heated to redness, a distinct crust of sulphide of arsenic was formed nearer to the heated portion than the deposit of sulphur. That the crust really consisted of sulphide of arsenic was proved by its solubility in carbonate of ammonia, and by its furnishing metallic arsenic when fused with carbonate of soda and cyanide of potassium in a current of carbonic acid. This experiment was repeated, with the same results, upon different samples of sulphide of iron and sulphuric acid. That the arsenic was due to the sulphide of iron, was ascertained by employing only so much of the purest sulphuric acid as gave no indication of arsenic in Marsh's process. Water saturated with the gas, when examined by Marsh's and the electrolytic test, was not found to contain arsenic.

No arsenic was detected in the washed hydrosulphuric acid gas prepared from native sulphide of antimony and hydrochloric acid.

On the Volumetric Relations of Ozone, and the Action of the Electrical Discharge on Oxygen and other Gases.

By Thomas Andrews, M.D., F.R.S., M.R.I.A., and Peter G. Tait, M.A.

(*From the Philosophical Transactions for* 1860.)*

1. The molecular changes produced by the electric current, or discharge, in certain compound bodies through which it is transmitted, furnish some of the most interesting examples of the action of a decomposing force that have been discovered in later times. The discharge of the Leyden jar, through fine wires or thin metallic leaves, exhibited long ago the heating power of the current, and the interesting experiments of the Dutch chemists afterwards showed that the disruptive discharge has the power of splitting up compound bodies into their constituent parts. The great invention of the pile of Volta, by furnishing an abundant supply of electricity of moderate tension, led subsequently to the important discovery of the polar decomposition of water and of other compound bodies. In the case of gases, it has been known, since the time of Priestly and Cavendish, that the spark-discharge has the apparently antagonistic properties of causing decomposition in some cases and combination in others. Finally, in our own day, Schönbein made the fine observation that a new substance (ozone), alike remarkable for the activity of its properties and for the facility with which it is destroyed, is formed by the action of the spark on pure oxygen gas, in the electrolysis of water, and in certain cases of slow oxidation.

Our object in the present communication is to continue the investigation, already begun by one of us,† of the properties of ozone, by subjecting it under varied conditions to a series of careful volumetric experiments. We hoped, in this way, to throw some new light on the relations of this singular body to oxygen, by determining whether any, and what, change of volume occurs in its formation. Our expectations in this respect have not been disappointed. We have ascertained that when oxygen changes into ozone, a great condensation takes place; so great indeed, that it is almost incompatible with the existence of ozone as an allotropic form of oxygen in the gaseous state. This investigation has naturally extended itself to an examination of the effects produced

* The substance of this paper was delivered as a Discourse to the Members of the Chemical Society of London by Dr Andrews.

† Philosophical Transactions, 1856, p. 1, or Quarterly Journal of the Chemical Society, ix, 16?

by the electrical discharge upon other gases, simple as well as compound; and although, from its great extent, this part of the inquiry has as yet been only partially entered into, some of the results already obtained are of considerable interest, and will be referred to in the present communication.

Before proceeding further, we must draw attention to the difference of action which, in many cases, we have found to exist between the spark, or spark-discharge, and the glow, or silent discharge. When the former terms are employed in this paper, they indicate a succession of brilliant sparks between two fine platinum wires, usually at the distance of 20 millims, (0·8 inch) from each other, and hermetically sealed into the tube containing the gas under observation. This form of discharge was obtained by connecting the free end of one of the platinum wires with an insulating stand, provided with a brass ball which was brought within a short distance of the prime conductor of an electrical machine in high order, while the free end of the other platinum wire was in connection with the ground. The silent discharge presented no visible character except a faint glow, not visible by daylight, at each metallic point, and was obtained by connecting the first platinum wire, not with the insulator, but directly with the prime conductor. To avoid the mixture of the "brush" with the silent discharge, it was necessary to establish the connection firmly both with the conductor and with the earth wire; and, in some cases, where a full effect was required, the machine had to be turned very slowly.

The electrical machine employed was a small plate one (18 inches in diameter), screwed down firmly to the floor of the apartment, opposite to an open fire. On the prolongation of the axis of the plate, a wheel, 6 inches in diameter, was fixed, from which a belt passed to an iron wheel, 40 inches in diameter, revolving in a wooden frame, which was also fastened to the floor. By this arrangement, the machine could be easily made to turn at the rate of 350 revolutions per minute. To maintain a regular and powerful stream of electricity at this rapid rate of motion, it was found necessary, in addition to the ordinary cushions, to hold with the hand against the plate a rubber covered with amalgam. When in ordinary working order, the machine gave above 600 sparks per minute, and in decomposing water produced in the same time 0·0002 cub. cent. of the mixed gases.*

The ordinary forms of eudiometrical apparatus were found to be wholly inapplicable to this inquiry. We failed in discovering, by their means, whether even a change of volume occurs, when ozone is produced from oxygen. To increase the difficulty, the

* Reports of the British Association for 1855, Trans. of Sect. p. 46.

experiments could not be carried on in presence of mercury or water, as the former is immediately attacked by ozone; and the latter not only destroys it rapidly by contact, but introduces a disturbing cause, in the form of aqueous vapour, exceeding in general the whole effect to be measured. In the apparatus now to be described these difficulties were overcome, and very minute changes of volume determined with certainty.

In figs. 1 and 2, the vessel in which the oxygen was contained is represented of different forms. It consists of a cylindrical tube *ab*, having two fine platinum wires hermetically sealed in opposite sides, and terminating in a capillary tube *cde*, of the form represented in the figure. The liquid in the limbs *d e*, is hydrated sulphuric acid (HO, SO_3), and it is by the changes

Fig. 1.

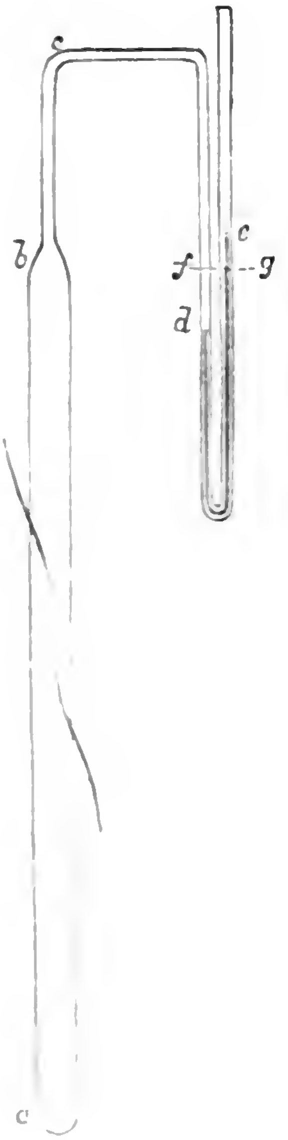


Fig. 2.

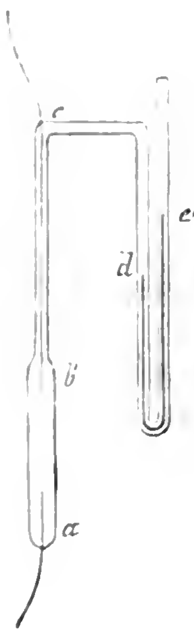
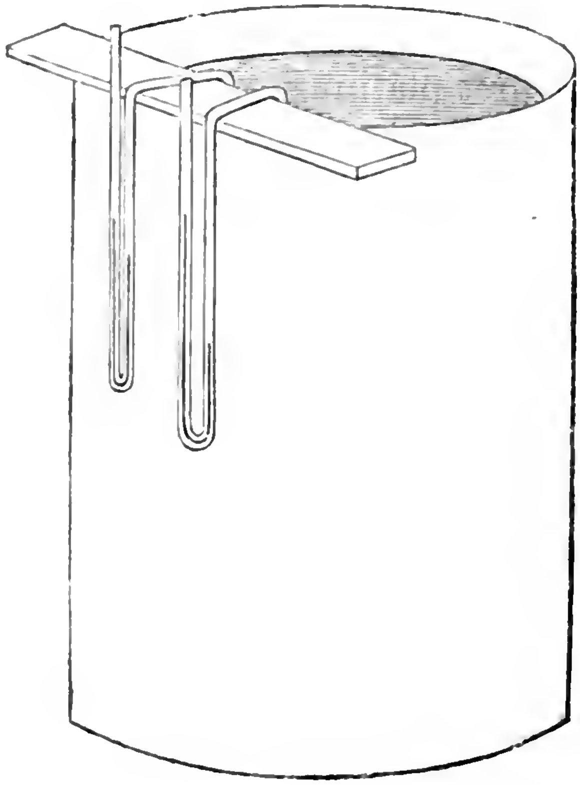


Fig. 3.

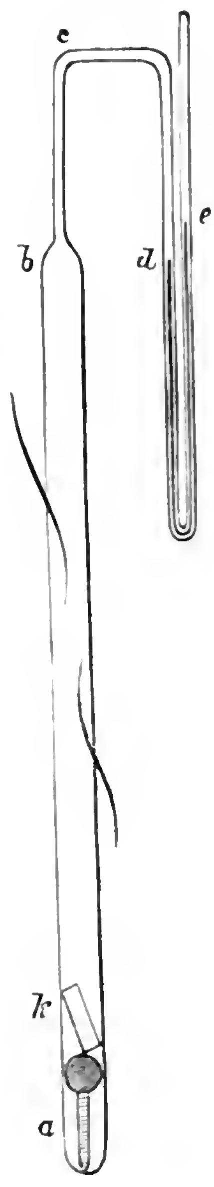


in the level of this liquid that the alteration in the volume of the gas in *abc* is determined. In order to make the necessary corrections for changes of temperature and pressure, during the interval between two observations, a vessel filled with dry air, of the same form and size as that employed in the experiment, was read along

with it; the reservoirs of both vessels being immersed in a large calorimeter, as shown in fig. 3. To the first of these vessels, we usually gave the name of *primary* vessel, and to the second that of *auxiliary* vessel. In order to correct for any slight difference in the size of the vessels, or in the diameters of the capillary tubes, simultaneous readings of both were made at different temperatures, and a coefficient thus determined, by means of which the indications of the two vessels could be afterwards accurately compared. When the reservoirs were large, the corrections so to be applied were frequently less than the errors of observation.

The extreme delicacy of this apparatus will be evident from the following considerations. If we take the case of a vessel with a large reservoir (fig. 1°), the changes in volume of the contained gas, supposing the temperature to remain constant, will be nearly proportional to the changes of pressure indicated by a barometer filled with sulphuric acid. As the height of such a barometer, at the mean pressure of the atmosphere, would be about 5500 millims., an alteration of 1 millim. in the difference of levels of the acid in the siphon tube (*de*, fig. 1) would correspond to a change of volume of about $\frac{1}{5000}$th of the entire gas; but, as it was easy to read to 0·5 millim., or even to 0·25 millim., the apparatus in this form enabled us to estimate a change of volume not exceeding one-half, or even one-fourth of that quantity. With a smaller reservoir (fig. 2), the indications of the apparatus were, it is true, not quite so delicate, and a careful set of comparative readings with the auxiliary vessel was always required; but even here, a change of volume amounting to not more than $\frac{1}{5000}$th of the whole, could be determined with certainty.

Fig 1°.



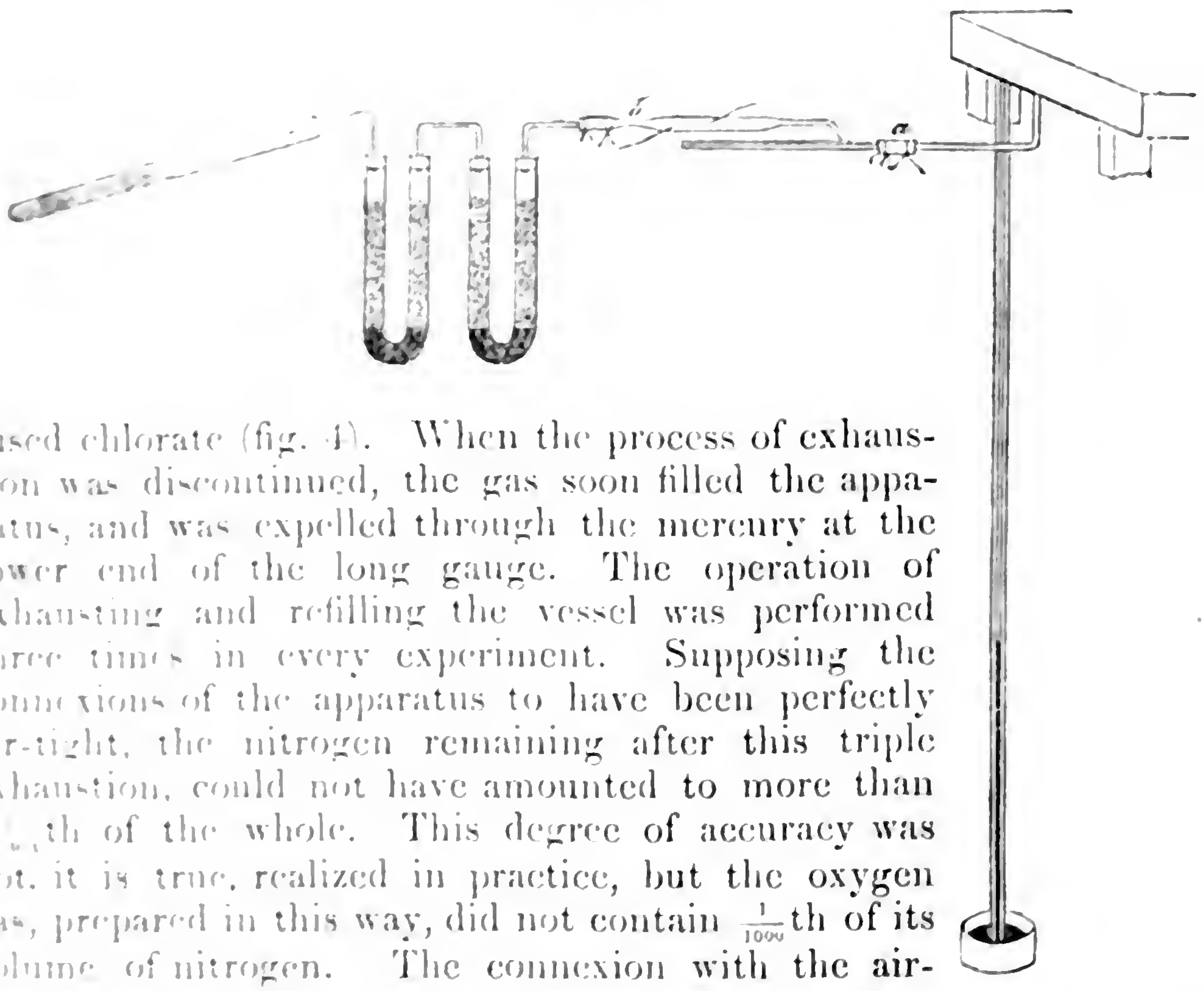
The absolute change of volume of the gas, corresponding to a given change in the levels of the acid in the siphon tube (corrected in the first instance by the aid of the auxiliary vessel), was estimated in two ways; first, by observing the change of level produced by raising or lowering the temperature of the water in the calorimeter through a small number of degrees; and secondly, by accurately determining, at the end of the experiment, the capacity of the reservoir and that of the capillary tube.

The form of apparatus now described can only be employed when the entire change of volume of the gas does not amount, in the course of the experiment, to more than about one-tenth of the

whole. When large changes of volume occur, the free end of the siphon tube must be hermetically sealed, so as to include a certain quantity of air, from whose subsequent change of volume that of the gas in the reservoir can be readily calculated. This modification of the apparatus we have found to be very convenient in experiments upon the action of the spark and silent discharge on the compound gases.

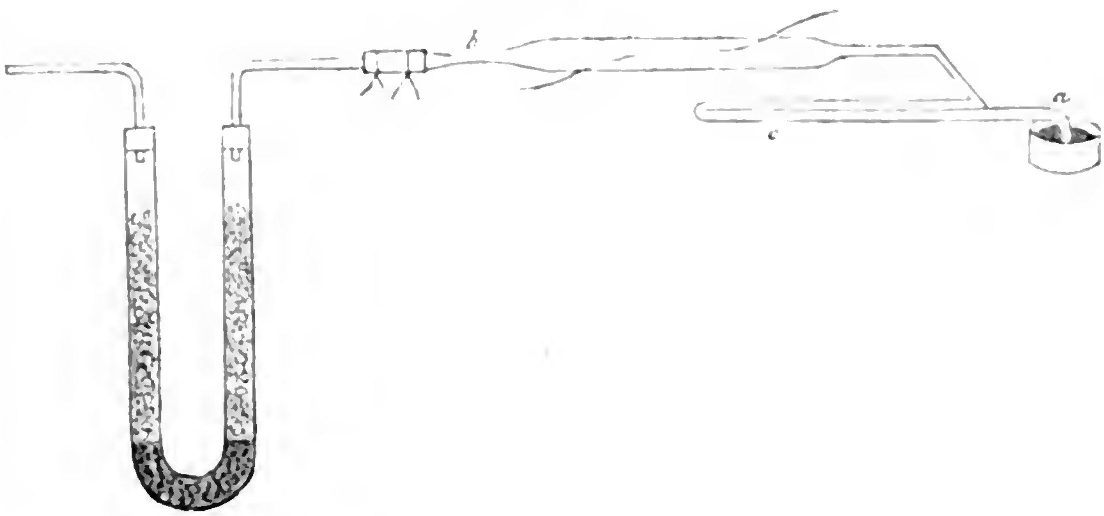
2. The oxygen gas employed in the following experiments was prepared from fused chlorate of potash, and, to purify and dry it, was passed through two U-tubes, the first containing fragments of marble moistened with a strong solution of caustic potash, the second, fragments of glass moistened with sulphuric acid. The potash-tube was sometimes suppressed. In order to remove every trace of nitrogen, the whole apparatus was placed in connexion with a good air-pump, and a vacuum produced to the extent of at least half an inch, while the gas was still being evolved from the

Fig. 4.



fused chlorate (fig. 4). When the process of exhaustion was discontinued, the gas soon filled the apparatus, and was expelled through the mercury at the lower end of the long gauge. The operation of exhausting and refilling the vessel was performed three times in every experiment. Supposing the connexions of the apparatus to have been perfectly air-tight, the nitrogen remaining after this triple exhaustion, could not have amounted to more than $\frac{1}{216000}$th of the whole. This degree of accuracy was not, it is true, realized in practice, but the oxygen gas, prepared in this way, did not contain $\frac{1}{1000}$th of its volume of nitrogen. The connexion with the air-pump at *a* having been broken (the gas still continuing to pass freely over), the end of the tube was softened in a lamp and bent downwards at an obtuse angle, so as to allow it to dip into sulphuric acid contained in a small dish, as shown

Fig. 5.



in fig. 5. The current of gas was now arrested, by removing gradually the lamps from the chlorate of potash, so as to allow the apparatus to cool slowly. When the acid had ascended a short way in *a c*, the vessel was sealed hermetically at *b*, and, after the acid had ascended to about the point *c*, the vessel was removed, and placed in the upright position represented in figs. 1 and 2. It was sometimes necessary to expel a bubble or two of gas, in order that the column of acid in the siphon tube might be in a convenient position when the vessel was placed in the calorimeter.

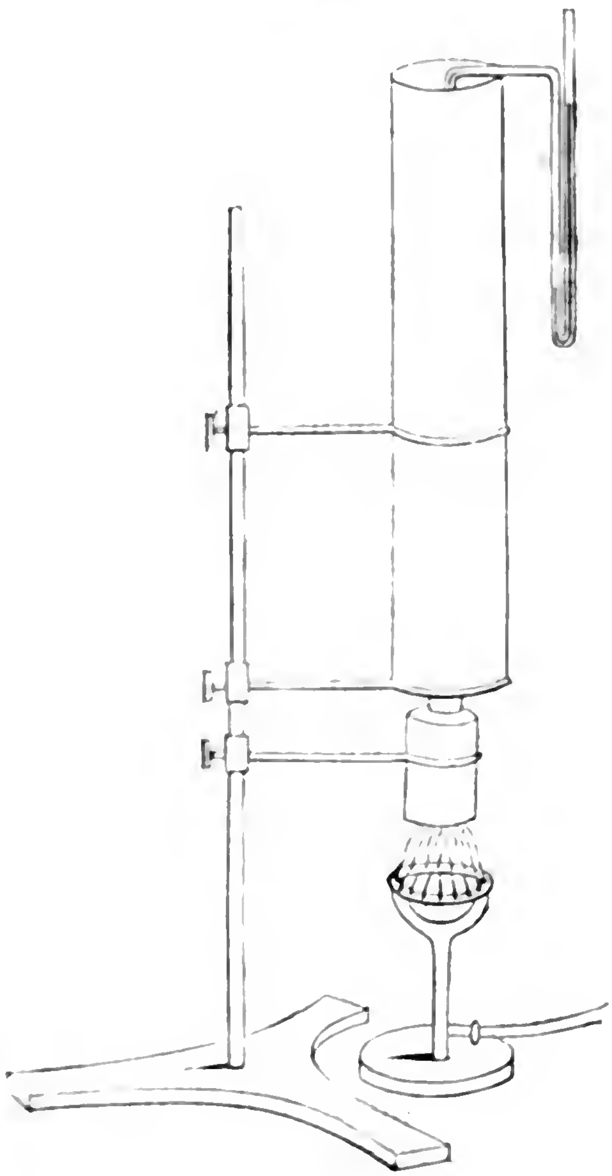
Previous to filling the vessels, they were always cleaned by means of boiling nitric acid, and subsequent washing with distilled water. They were afterwards carefully dried. To the success of several of the following experiments, this precaution was indispensable.

An auxiliary vessel having been filled in the same manner, either with air or with oxygen, the two vessels were placed in the calorimeter (fig. 3), and the difference of the levels of the acid in each carefully read. In our earlier experiments we generally used a cathetometer for this purpose, but latterly we found it more convenient and sufficiently accurate to apply to the limbs of the siphon tubes a scale divided into millimetres. From the rapidity indeed with which the readings were thus made, the results were found to be fully as trustworthy as those obtained with the cathetometer. When quantitative determinations were required, the temperature of the water in the calorimeter and the height of the barometer were carefully noted. After the levels were read, the free ends of the siphon tubes in both vessels were hermetically sealed. The primary vessel was then removed from the calorimeter and placed in connexion with the electrical machine, to be exposed to the action either of the spark or silent discharge. When this

operation was finished, the vessel was replaced in the calorimeter, the siphon tubes were opened, and the levels of the acid in the two vessels again read.

In order to examine the effects of heat, the reservoir of the vessel was placed in a sort of air-bath, formed by suspending a long copper cylinder above a LESLIE's gas-burner, the siphon tube being outside the cylinder, fig. 6. In this way a temperature

Fig. 6.



of 300° C., which was sufficient to destroy in a short time all the ozone reactions, was readily obtained. This temperature was estimated without difficulty, by observing the amount of compression of the air in the outer leg of the siphon tube. Our apparatus, with a slight modification, might, in fact, be employed as a thermometer for all temperatures below that at which glass begins to soften.

It will probably tend to perspicuity, if we state, before going further, some of the general results of our experiments on the action of the electrical discharge on pure oxygen.

I. When the silent discharge is passed through pure and dry oxygen, a contraction takes place. This contraction proceeds, at first rapidly, but afterwards more slowly, till it attains a limit, which, in one of our experiments, amounted to $\frac{1}{12}$th of the original volume of the gas.

II. If a few electrical sparks be passed through the gas in this contracted state, it expands till it recovers about three-fourths of the contraction; but, however long the sparks are passed, the gas never recovers its original volume.

III. When electrical sparks are passed through pure and dry oxygen, it contracts, but to a much smaller extent than when acted on by the silent discharge. The oxygen is, in fact, brought to the same volume as when electrical sparks are passed through the same gas, previously contracted by the silent discharge.

IV. When oxygen, contracted either by the silent discharge or by sparks, is exposed for a short time to the temperature of 270° C., it is restored to its original volume, and, on opening the vessel, the ozone reactions are found to have disappeared.

The following experiments, taken from a large number which gave similar results, will serve to illustrate the foregoing statements.

a. In a vessel, whose reservoir had a capacity of 5 cub. cent., sparks were passed for ten minutes, and produced a contraction of 5·9 millims., as measured by the change of levels of the acid in the siphon tube. By heating the vessel afterwards to 300° C., the levels were restored to within 0·1 millim. of their original position.

With the silent discharge in the same vessel, a contraction of 39·5 millims. (corresponding to about one-thirtieth of the volume of the gas) was obtained in ten minutes. Of this contraction heat restored 38·7 millims. This slight difference of 0·8 millim. is probably due to distortion of the vessel produced by heat.

Again, the silent discharge gave in ten minutes a contraction of 37·6 millims., of which sparks, subsequently passed for seven minutes, destroyed 29·7 millims., leaving 7·9 millims. undestroyed.

β. In another vessel having a reservoir of the capacity of 0·8 cub. cent., active sparks gave, in fifteen minutes, 4 millims. of contraction. After fifteen minutes more of sparks there was no additional contraction.

The silent discharge was now passed for fifteen minutes, and increased the contraction to 20 millims.; in fifteen minutes more, the entire contraction was 31 millims. Four strong sparks reduced this to 22·5 millims., six or seven more to 16 millims., seven more to 11 millims., and sparks, continued for ten minutes, left 4 millims. of permanent contraction.

γ. In a third vessel, of about the same capacity as the last, sparks gave a final contraction of 7·5 millims.; while the silent dis-

charge, pushed to its limit, increased the contraction to 90 millims. corresponding to about one-twelfth of the entire volume of the gas. This contraction was almost exactly destroyed by heat.

Before leaving this part of the subject, we should mention that, when a full contraction is obtained by means of the silent discharge, it will be found very slowly to diminish from day to day. We have not ascertained whether, at the end of a very long period of time, the original volume of the gas would be recovered. At 100° C., the contraction diminishes much more rapidly than at ordinary temperatures. Thus it appears that the state produced by the electrical discharge is not permanent, even at common temperatures, and that it becomes more unstable as the temperature rises, till at 270° C. it is rapidly destroyed.

We next proceeded to examine the volumetric changes which occur when oxygen contracted by the electrical discharge, is brought into contact with other bodies.

The first body we tried was *mercury*, the physical changes produced on which by ozone are known to be very remarkable. When a capsule containing this metal is broken in a tube of oxygen gas through which the silent discharge has been passed, the mercury instantly loses its mobility, and, if gently shaken, covers the interior of the tube with a brilliant mirror. As the action continues, the mirrored surface breaks up, and the coating becomes converted into a blackish semipulverulent substance. Unless the tube be very violently shaken, the ozone reactions will not be entirely destroyed, until the mercury has been for some hours in contact with the gas.

To determine the volumetric changes, a thin capsule, filled with pure mercury and hermetically sealed, was placed in a vessel with a large reservoir of the usual form (fig. 1°), which was afterwards filled with dry oxygen. After the levels had been read, the silent discharge was passed until a considerable contraction was obtained. The corrections for changes of temperature and pressure were, as in other cases, furnished by an auxiliary vessel. The free end of the siphon tube having been sealed, the primary vessel was removed from the calorimeter, and the capsule broken by a sudden jerk. The breaking of the capsule, in this and other experiments, was greatly facilitated by introducing into the vessel a small piece of thick glass tube, which fell on the capsule when the vessel was shaken (fig. 1°, *k*, p. 347).

Viewing ozone as an allotropic form of oxygen, in the gaseous state, we expected that when mercury came into contact with it, a contraction would take place, equal to the volume of the ozone which entered into combination with the metal. This anticipation has not been realized. After the rupture of the capsule, the vessel was

immediately replaced in the calorimeter and the levels read. Not the slightest diminution of volume was observed in any one of a large number of experiments; on the contrary, an increase, corresponding to a change of 1 millim. in the levels, generally occurred. On allowing the vessels to remain in the calorimeter, and reading the position of the acid in the siphon tubes from time to time, the gas was found to expand steadily, but slowly, for some hours, till from two-thirds to five-sixths of the contraction produced by the discharge was recovered. If the vessel was opened at any time while this expansion was going on, the ozone reactions were always manifest; but when the expansion was at an end, the ozone reactions had also ceased.

If the mercury, instead of being allowed tranquilly to act upon the gas, was violently agitated after breaking the capsule, a much smaller portion of the contraction was restored; in some cases not more than one-sixth.

Metallic *silver*, in the state both of leaf and of filings, gave similar results. The surface of the silver was partially blackened, about three-fourths of the original contraction was recovered, and the whole operation much more quickly terminated.

As the above reactions were evidently complex, the mercury and silver partly entering into combination with the gas, while the compounds formed appeared to exercise a catalytic action, we endeavoured to find an elementary body which would instantly destroy the ozone reactions, and at the same time be without action on dry oxygen. After some trials, we found that *iodine* possessed the required properties. We first ascertained that its vapour, although visible at common temperatures, has no appreciable tension. When a small capsule, containing pure and dry iodine, was broken in a vessel of the usual form filled with oxygen, the levels of the acid in the siphon tube were not altered. So slight also is the affinity of iodine for oxygen, that, on heating the reservoir so as to volatilize a considerable portion of the iodine, and afterwards allowing it to cool, the volume of the gas underwent no change. On the other hand, if ozone be present, the iodine is immediately attacked, a greyish-yellow compound is formed, and all ozone reactions are instantly destroyed.

The experiment already described with mercury was now repeated, substituting iodine for that metal. On breaking the capsule, the levels of the acid scarcely changed 1 millim., although the original contraction amounted to 50 millims. No subsequent expansion took place, and, on opening the vessel, the ozone reactions had entirely disappeared.

On the allotropic hypothesis, these experiments, and particularly the last, lead to the conclusion that ozone must have a density at least fifty times as great as that of oxygen. This conclusion is

indeed unavoidable from the experiments just described, unless it is assumed that at the same moment when one portion of the ozone combines with the iodine, another portion changes back into oxygen, and that these quantities are so related to one another, that the expansion due to the one is exactly equal to the contraction arising from the other. Such a supposition cannot, however, be considered probable.

4. In order to subject this remarkable property of ozone to a further examination, two additional series of experiments were undertaken, to a description of which we now proceed.

In the first series, a primary and an auxiliary vessel with large reservoirs were filled with pure and dry oxygen, small capsules hermetically sealed, and containing portions of the same solution of iodide of potassium, having been previously placed in each. The silent discharge was passed through the primary vessel so as to produce a considerable contraction, amounting in different experiments to from 40 millims. to 80 millims. The levels of the acid in the siphon tubes of both vessels having been carefully read while the vessels were in the calorimeter, the ends were sealed, and the vessels shaken so as to break the capsules in both. In the primary vessel, the iodide of potassium solution became instantly coloured dark brown from the iodine set free, while that in the auxiliary vessel did not change. On replacing the vessels in the calorimeter, and opening the ends of the siphon tubes, the change in the levels indicated a considerable expansion in both. In the auxiliary vessel, this expansion was due to the tension of the vapour of the solution of iodide of potassium alone; in the primary vessel, the expansion ought to have been less than this, on account of the absorption of ozone, if the volume of that body were capable of measurement.

In the following Table, which contains the results of five very careful experiments made in this way, the first column gives the amount of contraction produced by the silent discharge in the primary vessel, previous to the breaking of the capsules; the second, the temperature; the third and fourth, the respective expansions in the primary and auxiliary vessels; and the fifth, the differences of the numbers in the third and fourth columns:—

	mm.	°	mm.	mm.	mm.
I.	81·5	11·0C.	68·5	70.0	—1·5
II.	62·2	13·5C.	79·5	80·0	—0·5
III.	72·2	8·7C.	50·7	52·0	—1·3
IV.	63·5	12·2C.	71·5	73·0	—1·5
V.	45·5	16·2C.	87·0	89·2	—2·2

The capacity of the vessels employed in these experiments was about 30 cub. cent., and the primary and its auxiliary were found, in each experiment, by careful comparative observations, to work accurately together. The solution of iodide of potassium was purposely employed of different strengths in the several experiments. In I. it contained $\frac{1}{400}$th part of iodide of potassium; in II. $\frac{1}{200}$th; in III. $\frac{1}{3}$rd; and in IV. and V. $\frac{1}{5}$th. In the two last the solution was slightly acidulated with hydrochloric acid, in the others it was neutral. The capsules contained each about 0·7 grm. of these solutions.

The agreement in the results of these experiments, made with solutions of iodide of potassium so widely differing, is very remarkable. We ought also to observe that direct experiments, performed with great care, showed that the iodine set free by the ozone in the primary vessel did not affect the tension of the vapour of the solution.

Taking the mean of the above numbers, the density of ozone, as compared with that of oxygen, must be expressed, on the allotropic hypothesis, by about the number 60; in other words, ozone must be a gas only about six times lighter than the metal lithium. If the small differences in the fifth column be due, wholly or in part, to accidental causes, which is far from improbable, a still higher number must, on the same hypothesis, be taken to express the density of ozone.

In the last series of experiments, the amount of iodine set free in the solution of iodide of potassium was determined by analysis, and the weight of oxygen deduced therefrom compared with the weight of oxygen, calculated from the volumetric change which had occurred in the formation of the ozone.

We shall describe these experiments with some detail, particularly as the methods employed will be found applicable to other cases of gas analysis, where small changes in a given volume of gas have to be estimated.

Before filling it with oxygen, a sealed capsule containing a solution of iodide of potassium was introduced into the primary vessel, while the auxiliary contained the dry gas only. The silent discharge was passed through the former, and the contraction carefully observed. The capsule was then broken, and the solution agitated in the primary vessel for a few seconds. The siphon tube was next cut off, and the liquid carefully washed out and analysed by means of a weak solution of sulphurous acid, the exact strength of which had been immediately before determined by observing the amount required to decolorize a solution containing a known weight of iodine.

In some of the experiments the solution of iodide of potassium was slightly acidulated, in the others it was neutral. In the latter

case it was acidulated before being analysed. The results were the same, whether the solution was taken in the neutral or in the acid state. For although oxygen gas acts upon an acid solution of iodide of potassium, the action requires time, and the contact in this case was only continued for a few seconds.*

The formula by which we calculated the results of these experiments may be thus investigated:

Let f, g (fig. 1), be the mean level of the acid in the legs of the siphon tube; d, e, the levels at any time, t being the temperature, and Π the barometric pressure corrected for temperature. Let also $ge = fd = x$, and let H be the length of a tube similar to the siphon tube, and whose capacity is equal to that of the reservoir and of the siphon tube to f. Let a be the height of a barometer containing the liquid in the siphon tube, p the pressure of the gas in the vessel, and V the volume of the gas reduced to 0° C. and 760 millims.

Then evidently,

$$p \propto V \frac{1+at}{H+x}.$$

But

$$p = \Pi\left(1+\frac{2x}{a}\right),$$

hence

$$\frac{V(1+at)}{\Pi(H+x)\left(1+\frac{2x}{a}\right)}$$

is a constant quantity. Taking the logarithmic differential, we have

$$0=\frac{\delta V}{V}+\frac{a\delta t}{1+at}-\frac{\delta \Pi}{\Pi}-\frac{\delta x}{H+x}-\frac{\frac{2\delta x}{a}-\frac{2x\delta a}{a^2}}{1+\frac{2x}{a}}.$$

Now $\frac{\delta a}{a}=\frac{\delta \Pi}{\Pi}$ is multiplied by $\frac{x}{a}$, a quantity rarely exceeding $\frac{1}{200}$. To this degree of approximation, then, at least,

$$\frac{\delta V}{V}+\frac{a\delta t}{1+at}-\frac{\delta \Pi}{\Pi}=\delta x\left(\frac{2}{a}+\frac{1}{H}\right) \quad . \quad . \quad . \quad . \quad . \quad (1.)$$

* BAUMERT has objected on this ground to some of the experiments in a former communication made by one of us to the Society. We have found that, in the circumstances in which those experiments were performed, about one-twentieth of the effect was due to this cause; but as the oxygen acting on the solution of iodide of potassium set free its equivalent of iodine, the equality of the numbers given in that paper could not be disturbed by this action. We have, since that time, by additional experiments, fully confirmed the statement that no water is produced in the destruction of electrolytic ozone by heat.

If $V_,$, $H_,$, $x_,$ represent for the auxiliary vessel the quantities corresponding to V, H, x in the primary, we have, since $\delta V_, = 0$,

$$\frac{a\delta t}{1+at} - \frac{\delta H}{H} = \delta x_,\left(\frac{2}{a} + \frac{1}{H}\right) \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2.)$$

If $H_, = H$, *i. e.* if the primary and auxiliary vessels be of similar dimensions, we have at once, from (1.) and (2.),

$$\frac{\delta V}{V} = \delta x - \delta x_,\left(\frac{2}{a} + \frac{1}{H}\right) \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3.)$$

If the vessels be not similar, let

$$\delta x_,\left(\frac{2}{a} + \frac{1}{H_,}\right) = \delta x_{,,}\left(\frac{2}{a} = \frac{1}{H}\right),$$

then instead of (3.) we have

$$\frac{\delta V}{V} = (\delta x - \delta x_{,,})\left(\frac{2}{a} + \frac{1}{H}\right) \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4.)$$

Formula (3.) or (4.) gives the change of volume in the gas, as deduced from the observed change in the levels in the siphon tube.

For the estimation of the portion of the gas ($\delta_, V$) taken up as ozone by the solution of iodide of potassium, let C be the capacity of the primary vessel to f in litres, s the number of measures of sulphurous acid required to decolorize the solution when washed out of the vessel, S the number required to decolorize 1 grm. of iodine. Then we have, evidently, as a sufficient approximation,

$$\frac{\delta_, V}{V} = \frac{\dfrac{Is}{15{\cdot}8S}}{\dfrac{1{\cdot}4367Cp}{(1+at)760}}.$$

If we suppose ozone to be allotropic oxygen, with a relative density $e:1$, then $\delta_, V$ of oxygen contracts to $\frac{\delta_, V}{e}$ on being changed into ozone. Hence on this hypothesis,

$$\frac{\delta_, V}{\delta V} = \frac{e}{e-1}.$$

In order to verify this method, two similar vessels were filled with pure oxygen, one containing a capsule filled with a neutral solution of iodide of potassium, the other a capsule filled with an

acidulated solution of the same salt, and of precisely the same strength. The neutral solution was also introduced into the siphon tubes of both vessels. After breaking the capsules, the levels were read, and the vessels set aside for some days; at the end of which time it was found that a portion of oxygen gas had been absorbed in the primary vessel which contained the acid solution, while no change had occurred in the other. The levels were now read again, and the solution in the primary vessel analyzed.

The weight of the oxygen absorbed, as calculated by the foregoing formulæ from the volumetric change, was 0·0002188 grm., while its weight deduced from the analysis was 0·0002181 grm. The close agreement between these numbers shows that the method is susceptible of considerable accuracy.

The following Table contains the results of six experiments made in the manner above described. The primary and auxiliary vessels were carefully constructed of similar dimensions, and were found, on trial, to work accurately together, so that formula (3.) was directly applicable.

	I.	II.	III.	IV.	V.	VI.
	mm.	mm.	mm.	mm.	mm.	mm.
[illegible]	51·5	— 3·0	—18·5	—48·5	—51·0	39·0
[illegible]	31·0	18·0	— 2·25	— 6·5	— 9·75	— 8·25
[illegible]	4·0	38·5	— 0·5	16·5	72·5	65·0
[illegible]	— 7·0	— 2·75	—55·25	— 5·0	—39·0	—27·5
C	0·0239	0·0306	0·0288	0·0279	0·0269	0·0346
s	9·1	5·4	5·7	5·1	4·5	4·5
	grm.	grm.	grm.	grm.	grm.	grm.
L	0·0268	0·0684	0·0442	0·0674	0·0446	0·0621
S	22·6	47·95	30·85	49·5	36·8	44·43
	mm.	mm.	mm.	mm.	mm.	mm.
H	777·0	772·5	763·0	751·0	747·2	751·0
t	11°·0 C.	13°·45 C.	9°·1 C.	9°·8 C.	14°·0 C.	14°·7 C.
$\frac{1}{H}$	0·000025	0·000024	0·000025	0·000026	0·000027	0·000036
$\frac{V}{V'}$	0·972	0·938	0·947	0·927	0·952	0·933

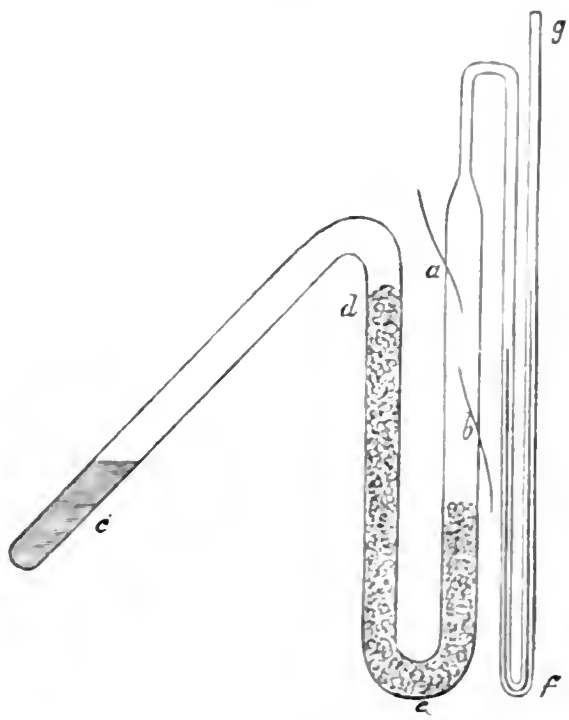
On comparing these experiments with the foregoing, it will be observed that they do not give exactly the same result. Interpreted as they stand, they indicate a density for ozone, if we may use the expression, more than infinite, inasmuch as the quantity of oxygen deduced from the analysis is less than that corresponding to the contraction observed. But, although every precaution was taken to avoid all sources of uncertainty, it is not improbable that this difference between the amount of oxygen deduced from the contraction and from the analysis may arise from a slight defect in some of the data, particularly as it would only involve an error of the order of $\frac{1}{2000}$th of the entire gas.

Taking the mean result of the three series of experiments as

they stand, it gives, on the allotropic hypothesis, almost exactly an infinite density for ozone.

5. The commonly received statement, that the whole of a given volume of dry oxygen gas can be converted into ozone by the passage of electrical sparks, is erroneous. In repeated trials, with tubes of different forms and sizes, we found that not more than one-twelfth of the oxygen could, under the most favourable circumstances, be converted into ozone, even by the silent discharge, and a much smaller proportion by the action of sparks. But if the ozone is removed as fast as it is produced, the conversion may be carried on indefinitely. An apparatus was constructed of the form shown in fig. 7. At *a*, *b* two fine platinum wires were hermetically

Fig. 7.



sealed into the glass; at *c* there was a solution of iodide of potassium, and *de* was filled with fragments of fused chloride of calcium which allowed the ozone to pass freely, but arrested the vapour of the solution; so that while the discharge always took place in pure and dry oxygen, the ozone was gradually absorbed. The volumetric change was measured by the readings of the sulphuric acid in the siphon tube *fg* sealed at *g*. The experiment was continued till five-twelfths of the oxygen (whose entire volume was about 12 cub. cent.) was absorbed, and the action was still going on. It was not considered necessary to persevere further, as the labour of turning the machine was very great. To produce the effect just mentioned, the discharge from the machine in excellent order had to be passed through the tube for twenty-four hours.

When the electrical discharge is passed through rarefied oxygen, the phenomena are apparently the same as with the gas at

the common pressure of the atmosphere. We filled a vessel with oxygen, and exhausted it till the pressure was equal to 1 inch of mercury, in the hope that in this rarefied state a larger portion of the oxygen might be converted into ozone than under greater pressures, but this did not prove to be the case. We intend on a future occasion to pursue this part of the inquiry, and to examine particularly the effects of the electrical discharge on oxygen in different states of rarefaction and condensation.

Ozone, obtained by electrolysis, gave results nearly similar to those already described. As the volume of the oxygen gas from which the ozone was derived could not, in the case of electrolytic ozone, be observed directly, it was estimated indirectly by placing three vessels in line, and passing the same stream of electrolytic oxygen through them all. By heating the first and last vessels to 300° C, and observing the expansion produced in each, it was easy to calculate the expansion which would have occurred in the middle vessel, if it had been exposed to similar treatment. This expansion was assumed to be equal to the contraction which occurs when ozone is produced from oxygen by means of the electrical discharge. Finally, the actual amount of ozone in the middle vessel was determined by introducing a solution of iodide of potassium, and ascertaining by analysis the amount of iodine set free. The individual experiments with electrolytic ozone did not agree so well with one another as those performed with ozone prepared by the discharge. This arose partly from the very small quantity of ozone in electrolytic oxygen, but chiefly from the irregularity in that quantity at different times, even when the current was passing very steadily, which made it difficult to ascertain with certainty the expansion due to the ozone in the middle vessel. Our earlier results, indeed, gave a measurable volume for ozone, and as a first approximation we obtained the number 4 as expressing its density.* But, by multiplying our experiments, and taking all possible precautions to ensure accuracy, we found that electrolytic ozone, like that produced by the discharge, has no appreciable volume.

Ozone is not condensed at common pressures by the cold produced by a mixture of solid carbonic acid and ether. A stream of electrolytic oxygen, passed very slowly, first through a U-tube surrounded by snow and salt, and next through a spiral tube immersed in the carbonic acid and ether bath ($-76°$ C.), underwent no change. The ozone reactions, as the gas issued from the tube, after exposure to this low temperature, were as strong as before it entered the bath.

* Proceedings of the Royal Society, vol. viii, p. 498, and vol. ix, p. 606.

6. *Hydrogen*, prepared with care by the action of dilute sulphuric acid recently boiled on zinc, and purified by passing through three U-tubes containing corrosive sublimate in solution, hydrate of potash, and sulphuric acid, respectively, and finally, in order to remove the last trace of oxygen, through a tube filled with metallic copper heated to redness, was found not to be altered in volume, either by the sparks or by the silent discharge. It appears to be a much better conductor of electricity than oxygen.

With *Nitrogen*, prepared in the usual way by depriving atmospheric air of its oxygen by means of heated copper, the results were also negative.

Among the compound gases, *Carbonic Acid* is rapidly decomposed by the spark, slowly by the silent discharge; in both cases expansion takes places.

Cyanogen is at once decomposed by the spark with deposition of carbon (?); but presents so great a resistance to the passage of electricity, that the action of the silent discharge could not be ascertained with certainty.

Protoxide of Nitrogen is readily attacked by the spark, with formation of hyponitric acid, whose characteristic red colour is distinctly seen. The primary result of the spark action is expansion, but on allowing the gas to stand, it gradually contracts, in consequence of the absorption of the hyponitric acid gas by the sulphuric acid in the siphon tube. It is impossible to determine the precise amount of the first expansion, as a certain amount of absorption occurs at the same time; but, in one imperfect trial, the ratio between the expansion and the subsequent contraction was nearly that of 1 : 2. This corresponds to the conversion of 8 vols. of protoxide of nitrogen into 4 vols. of hyponitric acid gas and 6 vols. of nitrogen. The silent discharge appears to produce the same result as the spark, but as the action is slower, the absorption interferes with any attempt to determine accurately the primary expansion.

Deutoxide of Nitrogen presents the interesting example of a compound gas, which, under the influence both of the spark and silent discharge, undergoes, like oxygen, a diminution of volume. This is independent of the subsequent absorption of the hyponitric acid formed. This gas is remarkable for the facility with which it is decomposed by both forms of discharge. The passage of sparks for two minutes, through a tube containing about 5 cub. cent., produced a contraction of the gas to nine-tenths of its original volume, followed after some time by a contraction not quite double of the former, from the absorption of the hyponitric acid gas. On continuing to pass sparks till the decomposition was finished, and waiting till the hyponitric acid gas was completely absorbed, the residue amounted to a little more than one-fourth of the original

gas. This residue consisted of a mixture of 11 vols. nitrogen, and 1 vol. oxygen. It is evident that the final result is a little complicated, but there can be little doubt that the action of the spark is to convert 8 vols. of deutoxide of nitrogen into 4 vols. of hyponitric acid gas, and 2 vols. of nitrogen. This decomposition may be due to the immediate action of the discharge; or the deutoxide of nitrogen may, in the first instance, be resolved into equal volumes of nitrogen and oxygen, the latter combining as it is formed with undecomposed deutoxide.

Carbonic Oxide has given results of great interest, the investigation of which has already occupied a considerable time, although it is not yet completed. The principal facts have, however, been already ascertained, and as they present some remarkable analogies to those already described in the case of oxygen, we shall briefly allude to them here, reserving the complete investigation for a future communication.

The carbonic oxide was prepared by heating oxalic acid with an excess of sulphuric acid, and absorbing the carbonic acid by means of a strong solution of hydrate of potash. The gas, as it escaped from the end of the apparatus, did not produce the slightest turbidity in lime or baryta water, and was completely absorbed by an ammoniacal solution of the subchloride of copper.

On exposing this gas to the action of the silent discharge, a steady contraction took place, and the surface of the positive platina wire became covered with a continuous deposit of a bronze colour. After some time, a trace, but only a trace, of the same deposit appeared at the point of the negative wire. If, after a contraction of 50 millims. or 60 millims. of the siphon tube had been obtained, a few electrical sparks were passed through the gas, the greater part of the contraction was, as in the case of oxygen, destroyed. Heat acted in the same direction, but did not restore the gas altogether to its original volume.

On continuing to pass the silent discharge, the gas continued to contract, and the deposit to increase on the positive wire. Portions of the same deposit were also scattered about the sides of the tube, being probably thrown off from the same wire. The experiment was in some cases continued till the gas had contracted to about one-third of its original volume. To effect this contraction, the machine had to be worked for sixty hours. The residual gas consisted of carbonic acid, oxygen, and undecomposed carbonic oxide. A similar deposit was obtained when the discharge took place between gold instead of platinum wires. This deposit appeared to be soluble in water. Its quantity was so small that direct analysis was altogether impossible. Its composition may, however, be determined by fixing with precision the ratios of the volumes of the carbonic acid and oxygen produced. We have suc-

ceeded in devising a method by which this analysis may be effected even with less than 0·5 cub. cent. of the mixed gases, but this part of the investigation is still unfinished.

Atmospheric Air is the only gaseous mixture which we have exposed to the action of the silent discharge. Like pure oxygen, it undergoes a diminution of volume; but the operation is more quickly terminated and the contraction is less than with that gas alone. If, after the passage of the discharge, the vessel be set aside for some hours, the contraction will be found to augment; and if the gaseous mixture be now again exposed to the action of the discharge, a further contraction will take place. On the other hand, heat destroys a portion only of the contraction at first produced. All these facts are easily explained from the simultaneous formation of ozone and of one of the higher oxides of nitrogen, and the marked influence of the latter, when formed, in arresting the formation of the former. To the same cause we have succeeded in referring an apparently anomalous state of oxygen, produced by passing a stream of strong electrical sparks for some minutes, through that gas containing a trace of nitrogen. The oxygen becomes by this treatment incapable of contracting or of changing into ozone under the action of the silent discharge, and only recovers its usual condition by exposure to heat or by standing for some hours. If the nitrogen amounts to not more than $\frac{1}{500}$th of the entire volume, this condition cannot be produced more than two or three times. At first we supposed it to be a new (passive) state of oxygen, but we have now no hesitation in referring it to the presence of a trace of hyponitric acid gas produced by the electrical sparks.

7. It is perhaps premature to attempt a positive explanation of the facts now described regarding ozone. The foregoing investigation into its volumetric relations has, for the moment, rather increased than diminished the difficulty of determining the true nature of that body. To reconcile the experimental results with the view that ozone is oxygen in an allotropic form, it is necessary to assume that its density immensely exceeds that of any known gas or vapour; being, as we have seen, according to the first and second series of experiments (§§ 3 and 4), from fifty to sixty times that of oxygen, and according to the third series (§ 4) absolutely infinite. Even the former results would make it only six times less dense than the metal lithium, and would place it rather in the class of solid or liquid bodies than of gaseous. The question may then be fairly proposed,—Can this singular body, at common temperatures be actually a solid or liquid substance, whose particles, in an extremely fine state of subdivision, are suspended in the oxygen with which it is always mixed? This question will scarcely, we think, admit of an affirmative answer. Not only does

ozone, mixed as usual with oxygen, pass through several U-tubes containing fragments of pumice moistened with sulphuric acid, but it exhibits its characteristic reactions when left for many hours in tubes of this kind. Besides, there is not the slightest cloud visible in a tube filled with oxygen, even when one-twelfth of the gas has been converted into ozone, nor does any deposit appear after long standing.

Ozone may be formed under conditions which exclude the possibility of its containing, as a constituent, any element except oxygen, or the elements of oxygen, if that body should hereafter be shown to be compound. As has been before stated, our experiments may be reconciled with the allotropic view and an ordinary density, but still one greater than that of oxygen, if we assume that when ozone comes into contact with such substances as iodine, or solutions of iodide of potassium, one portion of it, retaining the gaseous form, is changed back into common oxygen, while the remainder enters into combination; and that these are so related to one another, that the expansion due to the former is exactly equal to the contraction arising from the latter. We do not, however, consider this supposition to be by any means probable, nor can it be easily reconciled with the results (§ 3) obtained when mercury acts on ozone.

If we consider the conditions under which ozone is formed, we shall find them to be different from those which produce allotropic modifications in other cases. Such elements, for example, as phosphorus or sulphur, are modified by the action of heat, and not by the electrical discharge. It is true, at the same time, that the destruction of ozone, or, on the allotropic view, its reconversion into oxygen, by exposure to a temperature of 270° C., is apparently analogous to that action of heat whereby common phosphorus is converted into the red variety.

Without rejecting the allotropic constitution of ozone, although the results of our volumetric experiments are certainly difficult to reconcile with it, it may not be uninstructive to consider whether the facts already known admit of a different explanation. As ozone is formed from pure and dry oxygen by the electrical discharge, if it is not an allotropic form of oxygen, the latter must be either a mechanical mixture of two or more gases, or it must be a compound gas. It is perhaps scarcely necessary to consider the former hypothesis, according to which, oxygen, in its ordinary state, would be a mechanical mixture, as atmospheric air is a mixture of nitrogen and oxygen. The contraction, which occurs when the electrical discharge is passed through oxygen, is at first sight indeed favourable to such a supposition, inasmuch as the combination of gases is usually accompanied either by a diminution, or no change of volume. But we have not been able to

discover, in its other reactions, any facts which countenance this otherwise improbable view of the constitution of oxygen gas.

Finally, it remains to be considered, whether in the formation of ozone, oxygen does not undergo a more profound molecular change than is involved in an allotropic modification, whether, in short, this supposed element may not be actually decomposed. If, for the moment, we confine our attention to the phenomena which present themselves when the electrical discharge is passed through oxygen, this attractive hypothesis will be found to furnish a simple and plausible explanation of them all. It will be observed at once that the conditions under which ozone is formed from oxygen by the electrical discharge, are precisely those under which other gases, known to be compound, are decomposed. The electrical current is one of very high intensity, and therefore very favourable to decomposition: when passed in the form of the silent discharge, a large contraction takes place in the volume of the gas, which is partially destroyed by a few electrical sparks, and wholly by heat. With nitrogen and hydrogen no similar effects are observed, the volume of these gases being quite unaffected by either form of discharge.

The behaviour of carbonic oxide, when exposed to the action of the silent and spark discharge, corresponds remarkably to that of oxygen: the latter form of discharge, while producing itself only a limited contraction in carbonic oxide, destroying a part of the contraction produced by the former. Again when deutoxide of nitrogen is exposed to the action of the same agents, an immediate contraction takes place without any solid or liquid product being formed, showing that in certain cases of gaseous decompositions, the resulting gases occupy a smaller volume than the original compound.

If we assume that oxygen is resolved by the electrical discharge into a new compound (ozone), containing the same constituents as the oxygen itself, but in a different proportion, and into one of the constituents themselves, in the same manner as carbonic acid is resolved into carbonic oxide and oxygen, or nitric oxide into hyponitric acid and nitrogen, the results of our experiments will admit of an easy explanation. One of the simplest suppositions we can make for this purpose is, that two volumes of oxygen consist of one volume of U and one volume of V, united without condensation (U and V being the supposed constituents of oxygen), and that one volume of ozone consists of two volumes of U and one volume of V: and further, that by the action of heat, iodine, &c., ozone is resolved into U and oxygen.

The appearance of ozone at the positive pole in the electrolysis of water, and its formation by the agency of so active a body as ordinary phosphorus, do not seem unfavourable to its being the

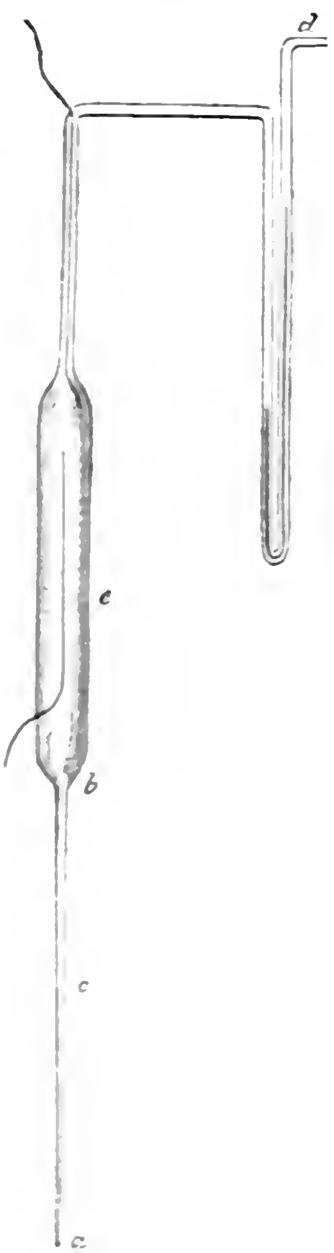
result of decomposition. But the same observation will not apply to its production by the action of acids on such bodies as the peroxide of barium. We certainly should not have expected to see a body derived from the decomposition of oxygen produced under the latter circumstances, and, although the facts connected with its production in these cases have not been studied with precision, yet there appears to be no doubt that ozone is actually formed.

We must in conclusion add, that the few attempts we have made to isolate either of the supposed constituents of oxygen have failed.

We are still continuing to prosecute this inquiry, and hope on a future occasion to lay before the Society the results of further experiments which are now in progress.

Note, added July 12, 1860.

Fig. 8.



It having been suggested that a certain amount of the contraction produced by the passage of the electrical discharge through tubes containing oxygen might arise from the action on that gas of the platinum wires, or of finely divided platinum, which, as in Mr. Gassiot's experiment, might be thrown off by the action of the discharge, we have made the following experiment, in order to ascertain whether such an action could have occurred in the conditions under which we operated. Before describing the experiment, it may be proper to state, that in the passage of the discharge of the electrical machine, there is no visible separation of metallic platinum, as in that of the discharge from the induction coil, nor other evidence of the wires being acted on; on the contrary, both the wires and tube retain their original appearance after having been frequently exposed to the alternate action of the discharge and of heat.

A vessel, of the form represented in the annexed figure, was filled with pure and dry oxygen. It differs from the tubes usually employed only by having the lower end of the reservoir drawn out into a capillary tube *a b*. The platinum wires were inserted as usual, and an auxiliary vessel of the same size and form was filled with dry air. After determining the comparative range of the two vessels, their

reservoirs were exposed, in the apparatus before described, to a temperature 300° C., in order to bring them as exactly as possible into the same condition. When they had cooled, the levels of the acid in the siphon tubes were again read, and the silent discharge was afterwards passed through the primary vessel till a contraction of twenty-seven millims. was obtained in its siphon tube. The extremity of the capillary tube of the reservoir was next cut off at *a*, and the end of the siphon tube *d*, which had the form represented in the figure, was dipped under sulphuric acid. The open end at *a*, was now connected with an apparatus, which supplied a slow stream of carefully dried air, and this was allowed to pass till the ozone and oxygen originally contained in the tube were entirely displaced by the dry air. It is obvious that by this arrangement the ozone was removed while the platinum wires and the inner surface of the tube were left in precisely the same state as after the passage of the discharge. The tube was next sealed off at *c*, by the application of the point of a fine blowpipe flame, the current having been arrested, so as to leave the usual column of sulphuric acid in the siphon tube. In sealing it, care was taken not to allow the air in *e* to become heated. The vessel was again placed, along with the auxiliary, in the calorimeter, and the levels read. The ends of the siphon tubes having been first sealed, the reservoirs were exposed to 300° C. An expansion should have taken place in the primary vessel, if the platinum had retained oxygen capable of being disengaged at 300° C.; but this was not found to be the case. The change of level in its sulphuric acid siphon (corrected by the auxiliary) did not amount to 0·2 millims., a degree of accuracy rarely attainable in these experiments.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

November 1st, 1860.

G. B. Buckton, Esq., in the Chair.

Rowlandson Cartmell, Esq., 81, High-street, Burton-on-Trent, was elected a Fellow of the Society.

Mr. H. C. Sorby laid before the meeting several specimens illustrating the artificial production of Pseudomorphs.

The following papers were read :—

"On the discrepancies in the statements of Pelouze and F. Mohr, respecting the solubility of Gallotannic acid in Ether," by Professor Bolley.

"On a hitherto unobserved source of Paraffin," by Professor Bolley.

The following donations were announced :—

"Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt in Wien," No. 4, for 1859: from the Institute.

"Jahrbuch der Central-Anstalt für Meteorologie und Erdmagnetismus in Wien," Band VI; from the Institute.

"Denkschriften der kaiserlichen Akademie der Wissenschaften in Wien," (math.-naturw. Classe), Band xviii.

"Sitzungsberichte derselben," Band xxxix, Hefte 1–5, und 1–12: from the Academy.

"Sitzungsberichte der königlich-baeyrischen Akademie der Wissenschaften," (math.-physikalische Classe) 1860, Hefte 1, 2: from the Academy.

"Bulletin de la Classe Physico-mathématique de l'Académie Impériale des Sciences de Saint Pétersbourg," Tome 1, Feuilles 10–36: from the Academy.

"Memorie dell' Academia delle Scienze dell' Istituto di Bologna," Tomi 8, 9, e Parti I, del Tomo 10.

"Rendiconti dell' Academia delle Scienze dell' Istituto di Bologna, 1857–58, e 1858–59:" from the Academy.

"Boletin de la Societa de Naturalistas en Nueva Granada," 1860: from the Society.

"American Journal of Science and Arts," for May, July and September, 1860: from the Editors.

"Journal of the Franklin Institute," June to October, 1860: from the Institute.

"Proceedings of the Academy of Natural Sciences at Philadelphia," 1860, Nos. 6–12: from the Academy.

"Proceedings of the American Philosophical Society," 1858, and January to June, 1859: from the Society.

"Smithsonian Report," for 1858: from the Smithsonian Institution.

"First Geological Report of Arkansas:" presented through the Smithsonian Institution, by the State of Arkansas.

"Canadian Journal," July to September, 1860: from the Canadian Institute.

"Memoirs of the Royal Astronomical Society," Vol. XXVIII.

"Monthly Notices of the Royal Astronomical Society," No. 9, for 1860: from the Society.

"Quarterly Journal of the Geological Society," No. 3, for 1860: from the Society.

"Chemical News," Nos. 29–44: from the Editor.

"Pharmaceutical Journal and Transactions," July to October 1860: from the Editor.

"Journal of the Society of Arts," Nos. 396 to 401, and 404 to 413: from the Society.

"Journal of the Photographic Society," July to October, 1860: from the Society.

"Literary Gazette," Nos. 105 to 121: from the Publishers.

"Proceedings of the Literary and Philosophical Society of Liverpool," 1859–60: from the Society.

"On the Lines of the Solar Spectrum," by Sir David Brewster, and Dr. J. H. Gladstone: from the Authors.

"On the Electric light of Mercury," by Dr. J. H. Gladstone: from the Author.

November 15th, 1860.

Professor Brodie, President, in the Chair.

The following Gentlemen were elected Fellows of the Society:—

J. H. Player, Esq., Oldbury, near Birmingham; A. Norman Tate, Esq., Runcorn Gap, near Warrington; Francis Valentine Paxton, Esq., B.A., Christchurch Oxford; George William Brown, Esq., 131, Sanchichall-street, Glasgow; Henry Brunner, Esq., Royal Institution Laboratory, Manchester.

The following papers were read:—

"On the crystalline form of Metallic Chromium," by Professor Bolley.

"On the colouring matter of Persian Berries," by Professor Bolley.

"On the basic Carbonates of Copper," by Mr. F. Field.

Dr. Hofmann made a communication "On the Separation of the Volatile Ethyl-alkaloids."

The following donations were announced:—

"Om Sövandets Bestanddele og deres Förderling i Havet," by G. Forchhammer: from the Author.

"Recherches sur les Rapports reciproques des Poids atomiques," par J. S. Stass: from the Author.

"Du Raisin considéré comme Médicament," par J. C. Herpin: from the Author.

"Bulletin de la Classe Physico-mathématique de l'Académie Impériale des Sciences de Saint Pétersbourg," Tome II, feuilles 1–17: from the Academy.

"Quarterly Journal of the Geological Society, No. 4," for 1860: from the Society.

"Elements of Chemistry," by William Allen Miller, Part II, "Inorganic Chemistry:" from the Author.

"On the Volumetric Relations of Ozone, and the action of the Electric Discharge on Oxygen and other Gases," by Thomas Andrews, and P. G. Tait: from the Authors.

"Chemical News," Nos. 46–49: from the Editor.

"Pharmaceutical Journal and Transactions," for November, 1860: from the Editor.

"Photographic Journal," for November, 1860: from the Photographic Society.

"Literary Gazette," Nos. 122, 123: from the Publishers.

"Notices of the Proceedings of the Meetings of the Members of the Royal Institution," 1859–60.

"List of Members, Officers, &c., of the Royal Institution," 1859.

"Additions to the Library of the Royal Institution," from July 1859, to July 1860: from the Royal Institution.

December 6th, 1860.

Col. Philip Yorke, Vice-President, in the Chair.

James Barratt, Esq., of Coniston, Windermere, Westmoreland, was elected a Fellow of the Society:—

A paper was read:

"On a new Lead-salt corresponding to Cobalt-yellow," by Mr. S. D. Hayes.

Dr. Hofmann made a communication "On the production of mixed Amines, Phosphines, and Arsines."

The following donations were announced:—

"Verhandlungen der naturforschenden Gesellschaft in Basel," 2th Theil, 4ter Heft: from the Society.

"Journal of the Franklin Institute," for November 1860: from the Institute.

"Journal of the Society of Arts," Nos. 414–419: from the Society.

"Pharmaceutical Journal and Transactions," for December, 1860: from the Society.

"Chemical News," Nos. 50–52: from the Editor.

"Literary Gazette," Nos. 125–127: from the Publishers.

"On the large Blasts at Holyhead," by George Robertson, Esq.: from the Author.

December 20th, 1860.

Professor Brodie, President, in the Chair.

The following were elected Fellows of the Society:—

Rev. W. R. Bowditch, Wakefield; John L. W. Thudichum, M.D., 65, South Audley Street.

The following papers were read:—

"Contributions to the Knowledge of the Laws of Gas-absorption," by Thomas H. Sims.

"On Sugar in Urine," by Dr. H. Bence Jones.

"On the Separation of Tellurium, Selenium and Sulphur," by Dr. Oppenheim.

"On Nitroprusside of Sodium," by Dr. Oppenheim.

The following donations were announced:—

"Abhandlungen der koniglich-baeyerischen Akademie der Wissenschaften (mathematisch-physikalische Classe)," Band VIII, Abtheilung 3.

"Sitzungsberichte derselben," 1860, Heft II.

"Denkrede an Alexander von Humboldt, gelesen in der öffentlichen Sitzung der königlich-baeyerischen Akademie der Wissenschaften," am 28 März, 1860, von C. F. P. von Martius: from the Royal Bavarian Academy of Sciences.

"Öfversight af Kongl. Vetenskaps-Akademiens Förhandlingar, sextonde Årgången," 1859: from the Swedish Academy of Sciences.

"American Journal of Science and Art," for November, 1860: from the Editors.

"Monthly Notices of the Royal Astronomical Society, Vol. XXI, No. 1: from the Society.

"Chemical News," Nos. 52–54: from the Editor.

"Journal of the Society of Arts," Nos. 420, 421: from the Society.

"Photographic Journal," for December, 1860: from the Photographic Society.

"Literary Gazette," Nos. 128, 129: from the Publishers.

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